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(54) Title: COMPOSITE ELEMENTS CONTAINING COMPACT POLYISOCYANATE POLYADDITION PRODUCTS

(54) Bezeichnung: VERBUNDELEMENTE ENTHALTEND KOMPAKTE POLYISOCYANAT–POLYADDITIONSPRODUKTE

(57) Abstract

The invention relates to composite elements with the following layer structure: (i) 2–20mm metal, (ii) 10–100 mm compact polyisocyanate polyaddition products obtained by reacting (a) isocyanates with (b) polyether polyalcohols, optionally in the presence of (c) catalysts and/or (d) auxiliary agents and/or additives, (iii) 2–20 mm metal.

(57) Zusammenfassung

Verbundelemente, die folgende Schichtstruktur aufweisen: (i) 2 bis 20 mm Metall, (ii) 10 bis 100 mm kompakte Polyisocyanat–Polyadditionsprodukte erhältlich durch Umsetzung von (a) Isocyanaten mit (b) Polyetherpolyalkoholen gegebenenfalls in Gegenwart von (c) Katalysatoren und/oder (d) Hilfs– und/oder Zusatzstoffen, (iii) 2 bis 20 mm Metall.

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Verbundelemente enthaltend kompakte Polyisocyanat-Polyadditionsprodukte

Beschreibung

Die Erfindung betrifft Verbundelemente, die folgende Schichtstruktur aufweisen:

(i) 2 bis 20 mm, bevorzugt 5 bis 20 mm, besonders bevorzugt 5 bis 10 mm Metall,

(ii) 10 bis 100 mm kompakte Polyisocyanat-Polyadditionsprodukte erhältlich durch Umsetzung von (a) Isocyanaten mit (b) Polyetherpolyalkoholen gegebenenfalls in Gegenwart von (c) Katalysatoren und/oder (d) Hilfs- und/oder Zusatzstoffen,

(iii) 2 bis 20 mm, bevorzugt 5 bis 20 mm, besonders bevorzugt 5 bis 10 mm Metall.

Des weiteren bezieht sich die Erfindung auf Verfahren zur Herstellung dieser Verbundelemente und deren Verwendung.

Für Konstruktion von Schiffen, beispielsweise Schiffsrümpfen und Laderaumabdeckungen, Brücken oder Hochhäusern müssen Konstruktionsteile verwendet werden, die erheblichen Belastungen durch äußere Kräfte standhalten können. Derartige Konstruktionsteile bestehen aufgrund dieser Anforderungen üblicherweise aus Metallplatten oder Metallträgern, die durch eine entsprechende Geometrie oder geeignete Verstrebungen verstärkt sind. So bestehen Schiffsrümpfe von Tankschiffen aufgrund von erhöhten Sicherheitsnormen üblicherweise aus einem inneren und einem äußeren Rumpf, wobei jeder Rumpf aus 15 mm dicken Stahlplatten, die durch ca. 2 m lange Stahlverstrebungen miteinander verbunden sind, aufgebaut ist. Da diese Stahlplatten erheblichen Kräften ausgesetzt sind, werden sowohl die äußere, als auch die innere Stahlhülle durch aufgeschweißte Verstärkungselemente versteift. Nachteilig an diesen klassischen Konstruktionsteilen wirken sich sowohl die erheblichen Mengen an Stahl aus, die benötigt werden, als auch die zeit- und arbeitsintensive Herstellung. Zudem weisen derartige Konstruktionsteile ein erhebliches Gewicht auf, wodurch sich eine geringere Tonnage der Schiffe und ein erhöhter Treibstoffbedarf ergibt. Zusätzlich sind solche klassischen Konstruktionselemente auf der Basis von Stahl sehr pflegeintensiv, da sowohl die

äußeren Oberfläche, als auch die Oberflächen der Stahlteile zwischen der äußeren und inneren Hülle regelmäßig gegen Korrosion geschützt werden müssen.

Der vorliegenden Erfindung lag daher die Aufgabe zugrunde, Konstruktionsteile zu entwickeln, die großen Belastungen durch äußere Kräfte standhalten und beispielsweise im Schiff-, Brücken- oder Hochhausbau Verwendung finden können. Die zu entwickelnden Konstruktionsteile, auch Verbundelemente genannt, sollen als Ersatz für bekannte Stahlkonstruktionen dienen und insbesondere Vorteile hinsichtlich Gewicht, Herstellprozeß und Wartungsintensität aufweisen. Insbesondere sollten die Verbundelemente mit großen Abmessungen einfach und schnell herzustellen sein und zudem durch eine verbesserte Stabilität gegen Hydrolyse im Schiffbau verwendbar sein.

Diese Aufgabe wurde erfindungsgemäß durch die eingangs beschriebenen Verbundelemente gelöst.

Die erfindungsgemäßen Verbundelemente werden unter Verwendung von Polyetherpolyalkoholen zur Umsetzung mit den Isocyanaten hergestellt. Die Verwendung von Polyetherpolyalkoholen bietet erhebliche Vorteile durch eine verbesserte Stabilität der Polyisocyanat-Polyadditionsprodukte gegen eine hydrolytische Spaltung und aufgrund der geringeren Viskosität, jeweils im Vergleich mit Polyesterpolyalkoholen. Die verbesserte Stabilität gegen Hydrolyse ist insbesondere bei einem Einsatz im Schiffbau vorteilhaft. Die geringere Viskosität der Polyetherpolyalkohole und der Reaktionsmischung zur Herstellung von (ii) enthaltend die Polyetherpolyalkohole ermöglicht eine schnellere und einfachere Befüllung des Raumes zwischen (i) und (iii) mit der Reaktionsmischung zur Herstellung der Verbundelemente. Aufgrund der erheblichen Abmessungen insbesondere von Konstruktionsteilen im Schiffbau sind niedrigviskose Flüssigkeiten von erheblichem Vorteil.

Die Herstellung der erfindungsgemäßen Verbundelemente kann man derart durchführen, daß man zwischen (i) und (iii) durch Umsetzung von (a) Isocyanaten mit (b) Polyetherpolyalkoholen gegebenenfalls in Gegenwart von (c) Katalysatoren und/oder (d) Hilfs- und/oder Zusatzstoffen kompakte Polyisocyanat-Polyadditionsprodukte herstellt, die an (i) und (iii) haften.

Bevorzugt kann man die Oberflächen von (i) und/oder (iii), an die (ii) nach der Herstellung der Verbundelemente haftet, mit Sand bestrahlen. Dieses Sandstrahlen kann nach üblichen Verfahren erfolgen. Beispielsweise kann man die Oberflächen unter hohem Druck mit üblichem Sand bestrahlen und damit beispielsweise reinigen

und Aufrauhen. Geeignete Apparaturen für eine solche Behandlung sind kommerziell erhältlich.

Durch diese Behandlung der Oberflächen von (i) und (iii), die nach der Umsetzung von (a) mit (b) gegebenenfalls in Gegenwart von (c) und/oder (d) in Kontakt mit (ii) stehen, führt zu einer deutlich verbesserten Haftung von (ii) an (i) und (iii). Das Sandstrahlen wird bevorzugt direkt vor der Einbringung der Komponenten zur Herstellung von (ii) in den Raum zwischen (i) und (iii) durchgeführt.

Nach der bevorzugten Behandlung der Oberflächen von (i) und (iii) werden diese Schichten bevorzugt in geeigneter Anordnung, beispielsweise parallel zueinander, fixiert. Der Abstand wird üblicherweise so gewählt, daß der Raum zwischen (i) und (iii) eine Dicke von 10 bis 100 mm aufweist. Die Fixierung von (i) und (iii) kann beispielsweise durch Abstandshalter erfolgen. Die Ränder des Zwischenraumes können bevorzugt derart abgedichtet werden, daß der Raum zwischen (i) und (iii) zwar mit (a) und (b) und gegebenenfalls (c) und/oder (d) gefüllt werden kann, ein Herausfließen dieser Komponenten aber verhindert wird. Das Abdichten kann mit üblichen Kunststoff- oder Metallfolien und/oder Metallplatten, die auch als Abstandshalter dienen können, erfolgen.

Die Schichten (i) und (iii) können bevorzugt als übliche Metallplatten, beispielsweise Stahlplatten, mit den erfindungsgemäßen Dicken eingesetzt werden.

Die Befüllung des Raumes zwischen (i) und (iii) kann sowohl in vertikaler Ausrichtung von (i) und (iii), als auch in horizontaler Ausrichtung von (i) und (iii) erfolgen.

Das Befüllen des Raumes zwischen (i) und (iii) mit (a), (b) und gegebenenfalls (c) und/oder (d) kann mit üblichen Fördereinrichtungen, bevorzugt kontinuierlich, durchgeführt werden, beispielsweise Hoch- und Niederdruckmaschinen, vorzugsweise Hochdruckmaschinen.

Die Förderleistung kann in Abhängigkeit des zu befüllenden Volumens variiert werden. Um eine homogene Durchhärtung von (ii) zu gewährleisten, wird die Förderleistung und Fördereinrichtung derart gewählt, daß der zu befüllende Raum innerhalb von 5 bis 20 min mit den Komponenten zur Herstellung von (ii) gefüllt werden kann.

Als Schichten (i) und (iii), üblicherweise Platten, können übliche Metalle verwendet werden, beispielsweise Eisen, üblicher Stahl, alle Arten von veredeltem Stahl, Aluminium und/oder Kupfer.

Sowohl (i) als auch (ii) können beschichtet, beispielsweise grundiert, lackiert und/oder mit üblichen Kunststoffen beschichtet bei der Herstellung der erfindungsgemäßen Verbundelemente eingesetzt werden. Bevorzugt werden (i) und (iii) unbeschichtet und besonders bevorzugt beispielsweise durch übliches Sandstrahlen gereinigt eingesetzt.

Die Herstellung der kompakten Polyisocyanat-Polyadditionsprodukten (ii), üblicherweise Polyurethan- und gegebenenfalls Polyisocyanuratprodukten, insbesondere Polyurethanelastomeren, durch Umsetzung von (a) Isocyanaten mit (b) gegenüber Isocyanaten reaktiven Verbindungen gegebenenfalls in Gegenwart von (c) Katalysatoren, (d) Hilfsmitteln und/oder Zusatzstoffen ist vielfach beschrieben worden. Unter kompakten Polyisocyanat-Polyadditionsprodukten sind solche zu verstehen, die keinen zelligen Aufbau aufweisen, wie er beispielsweise für Polyurethanschaumstoffe üblich ist. Um diesen kompakten Aufbau zu gewährleisten, wird die Zugabe von Treibmitteln zu den Ausgangskomponenten zur Herstellung von (ii) vermieden. Um einen Schäumprozeß weitestgehend zu vermeiden, sollten sowohl die Ausgangskomponenten (b) und gegebenenfalls (c) und (d) als auch die Oberflächen von (i) und (iii), die mit den Reaktionskomponenten in Berührung kommen, bevorzugt trocken sein.

Der Wassergehalt in der Reaktionsmischung enthaltend (a), (b) und gegebenenfalls (c) und/oder (d) beträgt bevorzugt 0 bis 0,03 Gew.-%, bezogen auf das Gewicht der Reaktionsmischung. Der Wassergehalt insbesondere in der Komponente (b) kann beispielsweise durch Destillation entsprechend eingestellt werden. Es ist zudem möglich, der Reaktionsmischung Verbindungen zuzugeben, die Wasser binden und damit eine Treibreaktion verhindern. Derartige Verbindungen, beispielsweise Molekularsiebe, sind allgemein bekannt. Z.B. können Silikate und Oxazolidine in geeigneter, bevorzugt fein verteilter Form verwendet werden. Diese Verbindungen können bevorzugt in Mengen von 0,05 bis 5 Gew.-%, bezogen auf das Gewicht der Reaktionsmischung, der Reaktionsmischung, bevorzugt der Komponente (b), zugesetzt werden.

Die Ausgangsstoffe (a), (b), (c) und (d) in dem erfindungsgemäßen Verfahren werden im Folgenden beispielhaft beschrieben:

Als Isocyanate (a) kommen die an sich bekannten aliphatischen, cycloaliphatischen, araliphatischen und/oder aromatischen Isocyanate, bevorzugt Diisocyanate in Frage, die gegebenenfalls nach allgemein bekannten Verfahren biuretisiert und/oder iscyanuratisiert worden sein können. Im einzelnen seien beispielhaft genannt: Alkylendiisocyanate mit 4 bis 12 Kohlenstoffatomen im Alkylenrest, wie 1,12-Dodecandiisocyanat, 2-Ethyl-tetramethylendiisocyanat-1,4, 2-Methylpentamethylendiisocyanat-1,5, Tetramethylendiisocyanat-1,4, Lysinesterdiisocyanate (LDI), Hexamethylendiisocyanat-1,6 (HDI), Cyclohexan-1,3- und/oder 1,4-diisocyanat, 2,4- und 2,6-Hexahydrotoluylendiisocyanat sowie die entsprechenden Isomerengemische, 4,4'-, 2,2'- und 2,4'-Dicyclohexylmethandiisocyanat sowie die entsprechenden Isomerengemische, 1-Isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexan (IPDI), 2,4- und/oder 2,6-Toluylendiisocyanat (TDI), 4,4'-, 2,4'- und/oder 2,2'-Diphenylmethandiisocyanat (MDI), Polyphenylpolymethylen-polyisocyanate und/oder Mischungen enthaltend mindestens zwei der genannten Isocyanate. Außerdem können Ester-, Harnstoff-, Allophanat-, Carbodiimid-, Uretdion- und/oder Urethangruppen enthaltende Di- und/oder Polyisocyanate in dem erfindungsgemäßen Verfahren eingesetzt werden. Bevorzugt werden 2,4`-, 2,2`- und/oder 4,4`-MDI und/oder Polyphenylpolymethylen-polyisocyanate eingesetzt, besonders bevorzugt Mischungen enthaltend Polyphenylpolymethylen-polyisocyanate und mindestens eines der MDI-Isomere.

Als (b) gegenüber Isocyanaten reaktive Verbindungen werden erfindungsgemäß Polyetherpolyalkohole, zweckmäßigerweise solche mit einer mittleren Funktionalität von 1 bis 8, vorzugsweise 1,5 bis 6, und einem Molekulargewicht von 400 bis 8000 verwendet.

Beispielsweise kommen als Polyetherpolyalkohole, die nach bekannter Technologie durch Anlagerung von Alkylenoxiden, beispielsweise Tetrahydrofuran, 1,3-Propylenoxid, 1,2- bzw. 2,3-Butylenoxid, Styroloxid und vorzugsweise Ethylenoxid und/oder 1,2-Propylenoxid an übliche Startersubstanzen erhältlich sind. Als Startersubstanzen können beispielsweise bekannte aliphatische, araliphatische, cycloaliphatische und/oder aromatische Verbindungen eingesetzt werden, mindestens eine Hydroxylgruppen und/oder mindestens eine Aminogruppen enthalten. Beispielsweise können als Startersubstanzen Ethandiol, Diethylenglykol, 1,2- bzw. 1,3-Propandiol, 1,4-Butandiol, 1,5-Pentandiol, 1,6-Hexandiol, 1,7-Heptandiol, Glycerin, Trimethylolpropan, Neopentylglykol, Zucker, beispielsweise Saccharose, Pentaerythrit, Sorbitol, Ethylendiamin, Propandiamin, Neopentandiamin, Hexamethylendiamin, Isophorondiamin, 4,4'-Diaminodicyclohexylmethan, 2-(Ethylamino)ethylamin, 3-(Methylamino)propylamin, Diethylen-

triamin, Dipropylentriamin und/oder N,N'-Bis(3-aminopropyl)-ethylendiamin.

Die Alkylenoxide können einzeln, alternierend nacheinander oder als Mischungen verwendet werden. Bevorzugt werden Alkylenoxide verwendet, die zu primären Hydroxylgruppen in dem Polyol führen. Besonders bevorzugt werden als Polyole solche eingesetzt, die zum Abschluß der Alkoxylierung mit Ethylenoxid alkoxyliert wurden und damit primäre Hydroxylgruppen aufweisen.

Gegebenenfalls können zusätzlich zu den Polyetherpolyalkoholen weitere gegenüber Isocyanaten reaktive Verbindungen als (b) verwendet werden, beispielsweise solche die als gegenüber Isocyanaten reaktive Gruppen Hydroxyl-, Thiol- und/oder primäre und/oder sekundäre Aminogruppen aufweisen, z.B. Polyole ausgewählt aus der Gruppe der Polyesterpolyalkohole, Polythioether-polyole, hydroxylgruppenhaltigen Polyacetale und hydroxylgruppenhaltigen aliphatischen Polycarbonate oder Mischungen aus mindestens zwei der genannten Polyole. Diese gegebenenfalls zusätzlich zu den Polyetherpolyalkoholen einzusetzenden Verbindungen weisen üblicherweise eine Funktionalität von 2 bis 6 und ein Molekulargewicht von 400 bis 8000 auf.

Geeignete Polyesterpolyole können beispielsweise aus organischen Dicarbonsäuren mit 2 bis 12 Kohlenstoffatomen, vorzugsweise aliphatischen Dicarbonsäuren mit 4 bis 6 Kohlenstoffatomen, und mehrwertigen Alkoholen, vorzugsweise Diolen, mit 2 bis 12 Kohlenstoffatomen, vorzugsweise 2 bis 6 Kohlenstoffatomen hergestellt werden. Die Polyesterpolyole besitzen vorzugsweise eine Funktionalität von 2 bis 4, insbesondere 2 bis 3, und ein Molekulargewicht von 480 bis 3000, vorzugsweise 600 bis 2000.

Als gegenüber Isocyanaten reaktive Verbindungen sind zusätzlich zu den erfindungsgemäßen Polyetherpolyalkoholen des weiteren Substanzen geeignet, die ein Kohlenwasserstoffgerüst mit 10 bis 40 Kohlenstoffatomen und 2 bis 4 gegenüber Isocyanaten reaktive Gruppen aufweisen. Unter dem Ausdruck Kohlenwasserstoffgerüst ist eine ununterbrochene Abfolge von Kohlenstoffatomen zu verstehen, die nicht wie beispielsweise im Falle von Ethern mit Sauerstoffatomen unterbrochen ist. Als solche Substanzen, im Folgenden auch als (b3) bezeichnet, können beispielsweise Rizinusöl und deren Derivate eingesetzt werden.

Als gegenüber Isocyanaten reaktive Verbindungen können des weiteren zusätzlich zu den erfindungsgemäßen Polyetherpolyalkoholen gegebenenfalls Diole und/oder Triole mit Molekulargewichten von 60 bis <400 als Kettenverlängerungs- und/oder Vernetzungsmittel

bei dem erfindungsgemäßen Verfahren eingesetzt werden. Zur Modifizierung der mechanischen Eigenschaften, z.B. der Härte, kann sich jedoch der Zusatz von Kettenverlängerungsmitteln, Vernetzungsmitteln oder gegebenenfalls auch Gemischen davon als vorteilhaft erweisen. Die Kettenverlängerungs- und/oder Vernetzungsmittel weisen vorzugsweise ein Molekulargewicht von 60 bis 300 auf. In Betracht kommen beispielsweise aliphatische, cycloaliphatische und/ oder araliphatische Diole mit 2 bis 14, vorzugsweise 4 bis 10 Kohlenstoffatomen, wie z.B. Ethylenglykol, Propandiol-1,3, Decandiol-1,10, o-, m-, p-Dihydroxycyclohexan, Diethylenglykol, Dipropylenglykol und vorzugsweise Butandiol-1,4, Hexandiol-1,6 und Bis-(2-hydroxy-ethyl)-hydrochinon, Triole, wie 1,2,4-, 1,3,5-Trihydroxy-cyclohexan, Glycerin und Trimethylolpropan, niedermolekulare hydroxylgruppenhaltige Polyalkylenoxide auf Basis Ethylen- und/oder 1,2-Propylenoxid und den vorgenannten Diolen und/oder Triolen als Startermoleküle und/oder Diamine wie z.B. Diethyltoluendiamin und/oder 3,5-Dimethylthio-2,4-toluenediamin.

Sofern zur Herstellung der Polyisocyanat-Polyadditionsprodukten Kettenverlängerungsmittel, Vernetzungsmittel oder Mischungen davon Anwendung finden, kommen diese zweckmäßigerweise in einer Menge von 0 bis 30 Gew.-%, vorzugsweise von 2 bis 20 Gew.-%, bezogen auf das Gewicht der insgesamt eingesetzten gegenüber Isocyanaten reaktiven Verbindungen (b), zum Einsatz.

Außerdem können zusätzlich zu den erfindungsgemäßen Polyetherpolyalkoholen aliphatische, araliphatische, cycloaliphatische und/ oder aromatische Carbonsäuren zur Optimierung des Härtungsverlaufes bei der Herstellung von (ii) eingesetzt werden. Beispiele für solche Carbonsäuren sind Ameisensäure, Essigsäure, Bernsteinsäure, Oxalsäure, Malonsäure, Glutarsäure, Adipinsäure, Zitronensäure, Benzoesäure, Salicylsäure, Phenylessigsäure, Phthalsäure, Rizinolsäure, Toluolsulfonsäure, Derivate der genannten Säuren, Isomere der genannten Säuren und beliebigen Mischungen der genannten Säuren. Der Gewichtsanteil dieser Säuren kann 0 bis 5 Gew.-%, bevorzugt 0,2 bis 2 Gew.-%, bezogen auf das Gesamtgewicht von (b), betragen.

Bevorzugt setzt man als (b) eine Mischung ein, die enthält:

(b1) 40 bis 99 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 1,5 bis 2,99 und einem mittleren Molekulargewicht von 400 bis 8000 und

(b2) 1 bis 60 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 3 bis 5 und einem mittleren Molekulargewicht von 150 bis 8000.

Besonders bevorzugt setzt man als (b) eine Mischung ein, die enthält:

(b1) 40 bis 98 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 1,5 bis 2,99 und einem mittleren Molekulargewicht von 400 bis 8000,

(b2) 1 bis 60 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 3 bis 5 und einem mittleren Molekulargewicht von 150 bis 8000 und

(b3) 1 bis 50 Gew.-% mindestens einer gegenüber Isocyanaten reaktiven Verbindung, die ein Kohlenwasserstoffgerüst mit 10 bis 40 Kohlenstoffatomen und 2 bis 4 gegenüber Isocyanaten reaktive Gruppen aufweist.

Insbesondere können die genannten, bevorzugten Mischungen zusätzlich die bereits genannten Carbonsäuren enthalten.

Bevorzugt ist das Gewichtsverhältnis von Polyetherpolyalkoholen zu Polyesterpolyalkoholen in der Komponente (b) >100, besonders bevorzugt >1000, insbesondere werden zur Herstellung von (ii) keine Polyesterpolyalkohole als (b) eingesetzt.

Mit dem Einsatz von Amin-gestarteten Polyetherpolyalkoholen kann zudem das Durchhärteverhalten von der Reaktionsmischung zur Herstellung von (ii) verbessert werden. Bevorzugt werden die Verbindungen (b), wie auch die Komponenten (c) und (d), mit einem möglichst geringen Gehalt an Wasser eingesetzt, um die Bildung von Kohlendioxid durch Reaktion des Wassers mit Isocyanatgruppen zu vermeiden.

Als Katalysatoren (c) können allgemein bekannte Verbindungen eingesetzt werden, die die Reaktion von Isocyanaten mit den gegenüber Isocyanaten reaktiven Verbindungen stark beschleunigen, wobei vorzugsweise ein Gesamtkatalysatorgehalt von 0,001 bis 15 Gew.-%, insbesondere 0,05 bis 6 Gew.-%, bezogen auf das Gewicht der insgesamt eingesetzten gegenüber Isocyanaten reaktiven Verbindungen, verwendet wird. Beispielsweise können folgende Verbindungen verwendet werden: Triethylamin, Tributylamin, Dimethylbenzylamin, Dicyclohexylmethylamin, Dimethylcyclohexylamin, N,N,N',N'-Tetramethyl-diamino-diethylether, Bis-(dimethylaminopropyl)-harnstoff, N-Methyl- bzw. N-Ethylmorpholin, N-Cyclo-

hexylmorpholin, N,N,N',N'-Tetramethylethylendiamin, N,N,N',N'-Tetramethylbutandiamin, N,N,N',N'-Tetramethylhexandiamin-1,6, Pentamethyldiethylentriamin, Dimethylpiperazin, N-Dimethylaminoethylpiperidin, 1,2-Dimethylimidazol, 1-Azabicyclo-(2,2,0)-octan, 1,4-Diazabicyclo-(2,2,2)-octan (Dabco) und Alkanolaminverbindungen, wie Triethanolamin, Triisopropanolamin, N-Methyl- und N-Ethyl-diethanolamin, Dimethylaminoethanol, 2-(N,N-Dimethylaminoethoxy)ethanol, N,N',N''-Tris-(dialkylaminoalkyl)hexahydrotriazine, z.B. N,N',N''-Tris-(dimethylaminopropyl)-s-hexahydrotriazin, Eisen(II)-chlorid, Zinkchlorid, Bleioctoat und vorzugsweise Zinnsalze, wie Zinndioctoat, Zinndiethylhexoat, Dibutylzinndilaurat und/oder Dibutyldilaurylzinnmercaptid, 2,3-Dimethyl-3,4,5,6-tetrahydropyrimidin, Tetraalkylammoniumhydroxide, wie Tetramethylammoniumhydroxid, Alkalihydroxide, wie Natriumhydroxid, Alkalialkoholate, wie Natriummethylat und Kaliumisopropylat, und/oder Alkalisalze von langkettigen Fettsäuren mit 10 bis 20 C-Atomen und gegebenenfalls seitenständigen OH-Gruppen.

Es hat sich als sehr vorteilhaft erwiesen, die Herstellung von (ii) in Gegenwart von (c), um die Reaktion zu beschleunigen, durchzuführen.

Der Reaktionsmischung zur Herstellung der Polyisocyanat-Polyadditionsprodukte (ii) können gegebenenfalls (d) Hilfsmittel und/oder Zusatzstoffe einverleibt werden. Genannt seien beispielsweise Füllstoffe, oberflächenaktive Substanzen, Farbstoffe, Pigmente, Flammschutzmittel, Hydrolyseschutzmittel, fungistatische und bakteriostatisch wirkende Substanzen.

Als oberflächenaktive Substanzen kommen z.B. Verbindungen in Betracht, welche zur Unterstützung der Homogenisierung der Ausgangsstoffe dienen und gegebenenfalls auch geeignet sind, die Zellstruktur der Kunststoffe zu regulieren. Genannt seien beispielsweise Emulgatoren, wie die Natriumsalze von Ricinusölsulfaten oder von Fettsäuren sowie Salze von Fettsäuren mit Aminen, z.B. ölsaures Diethylamin, stearinsaures Diethanolamin, ricinolsaures Diethanolamin, Salze von Sulfonsäuren, z.B. Alkali- oder Ammoniumsalze von Dodecylbenzol- oder Dinaphthylmethandisulfonsäure und Ricinolsäure. Die oberflächenaktiven Substanzen werden üblicherweise in Mengen von 0,01 bis 5 Gew.-%, bezogen auf 100 Gew.-% der insgesamt eingesetzten gegenüber Isocyanaten reaktiven Verbindungen (b), angewandt.

Geeignete Flammschutzmittel sind beispielsweise Trikresylphosphat, Tris-(2-chlorethyl)phosphat, Tris-(2-chlorpropyl)phosphat, Tris(1,3-dichlorpropyl)phosphat, Tris-(2,3-dibrompropyl)phosphat, Tetrakis-(2-chlorethyl)-ethylendiphosphat, Dimethylmethanphosphonat, Diethanolaminomethylphosphonsäurediethylester sowie handelsübliche halogenhaltige Flammschutzpolyole. Außer den bereits genannten halogensubstituierten Phosphaten können auch anorganische oder organische Flammschutzmittel, wie roter Phosphor, Aluminiumoxidhydrat, Antimontrioxid, Arsenoxid, Ammoniumpolyphosphat und Calciumsulfat, Blähgraphit oder Cyanursäurederivate, wie z.B. Melamin, oder Mischungen aus mindestens zwei Flammschutzmitteln, wie z.B. Ammoniumpolyphosphaten und Melamin sowie gegebenenfalls Maisstärke oder Ammoniumpolyphosphat, Melamin und Blähgraphit und/oder gegebenenfalls aromatische Polyester zum Flammfestmachen der Polyisocyanat-polyadditionsprodukte verwendet werden. Im allgemeinen hat es sich als zweckmäßig erwiesen, 5 bis 50 Gew.-%, vorzugsweise 5 bis 25 Gew.-%, der genannten Flammschutzmittel, bezogen auf das Gewicht der insgesamt eingesetzten gegenüber Isocyanaten reaktiven Verbindungen, zu verwenden.

Als Füllstoffe, insbesondere verstärkend wirkende Füllstoffe, sind die an sich bekannten, üblichen organischen und anorganischen Füllstoffe, Verstärkungsmittel, Beschwerungsmittel, Mittel zur Verbesserung des Abriebverhaltens in Anstrichfarben, Beschichtungsmittel usw. zu verstehen. Im einzelnen seien beispielhaft genannt: anorganische Füllstoffe wie silikatische Mineralien, beispielsweise Schichtsilikate wie Antigorit, Serpentin, Hornblenden, Amphibole, Chrisotil und Talkum, Metalloxide, wie Kaolin, Aluminiumoxide, Titanoxide und Eisenoxide, Metallsalze, wie Kreide, Schwerspat und anorganische Pigmente, wie Cadmiumsulfid und Zinksulfid, sowie Glas u.a.. Vorzugsweise verwendet werden Kaolin (China Clay), Aluminiumsilikat und Copräzipitate aus Bariumsulfat und Aluminiumsilikat sowie natürliche und synthetische faserförmige Mineralien wie Wollastonit, Metall- und Glasfasern geringer Länge. Als organische Füllstoffe kommen beispielsweise in Betracht: Kohle, Melamin, Kollophonium, Cyclopentadienylharze und Pfropfpolymerisate sowie Cellulosefasern, Polyamid-, Polyacrylnitril-, Polyurethan-, Polyesterfasern auf der Grundlage von aromatischen und/oder aliphatischen Dicarbonsäureestern und insbesondere Kohlenstoffasern. Die anorganischen und organischen Füllstoffe können einzeln oder als Gemische verwendet werden.

Bevorzugt setzt man bei der Herstellung von (ii) 10 bis 70 Gew.-% Füllstoffe, bezogen auf das Gewicht von (ii), als (d) Hilfs- und/oder Zusatzstoffe ein. Als Füllstoffe verwendet man bevorzugt

Talkum, Kaolin, Calziumcarbonat, Schwerspat, Glasfasern und/oder Mikroglaskugeln. Die Größe der Partikel der Füllstoffe ist bevorzugt so zu wählen, daß das Eintragen der Komponenten zur Herstellung von (ii) in den Raum zwischen (i) und (iii) nicht behindert wird. Besonders bevorzugt weisen die Füllstoffe eine Partikelgröße von < 0,5 mm auf.

Die Füllstoffe werden bevorzugt in Mischung mit der Polyolkomponente bei der Umsetzung zur Herstellung der Polyisocyanat-Polyadditionsprodukte eingesetzt.

Die Füllstoffe können dazu dienen, den im Vergleich beispielsweise zum Stahl größeren thermischen Ausdehnungskoeffizient der Polyisocyanat-Polyadditionsprodukte zu verringern und damit dem des Stahls anzupassen. Dies für einen nachhaltig festen Verbund zwischen den Schichten (i), (ii) und (iii) besonders vorteilhaft, da damit geringere Spannungen zwischen den Schichten bei thermischer Belastung auftreten.

Das Gewicht von (ii) entspricht per Definition dem Gewicht der zur Herstellung von (ii) eingesetzten Komponenten (a), (b) und gegebenenfalls (c) und/oder (d).

Zur Herstellung der erfindungsgemäßen Polyisocyanat-Polyadditionsprodukte werden die Isocyanate und die gegenüber Isocyanaten reaktiven Verbindungen in solchen Mengen zur Umsetzung gebracht, daß das Äquivalenzverhältnis von NCO-Gruppen der Isocyanate zur Summe der reaktiven Wasserstoffatome der gegenüber Isocyanaten reaktiven Verbindungen 0,85 bis 1,25 : 1, vorzugsweise 0,95 bis 1,15 : 1 und insbesondere 1 bis 1,05 : 1, beträgt. Falls (ii) zumindest teilweise Isocyanuratgruppen gebunden enthalten, wird üblicherweise ein Verhältnis von NCO-Gruppen zur Summe der reaktiven Wasserstoffatome von 1,5 bis 60 : 1, vorzugsweise 1,5 bis 8 : 1, angewandt.

Die Polyisocyanat-Polyadditionsprodukte werden üblicherweise nach dem one shot-Verfahren oder nach dem Prepolymerverfahren, beispielsweise mit Hilfe der Hochdruck- oder Niederdruck-Technik hergestellt.

Als besonders vorteilhaft hat es sich erwiesen, nach dem Zweikomponentenverfahren zu arbeiten und die gegenüber Isocyanaten reaktiven Verbindungen (b), gegebenenfalls die Katalysatoren (c) und/oder Hilfs- und/oder Zusatzstoffe sowie Füllstoffe (d) in der Komponente (A) zu vereinigen und bevorzugt innig miteinander zu vermischen und als Komponente (B) die Isocyanate zu verwenden.

Die Ausgangskomponenten werden üblicherweise bei einer Temperatur von 0 bis 100°C, vorzugsweise von 20 bis 60°C, gemischt und wie bereits beschrieben in den Raum zwischen (i) und (iii) eingebracht. Die Vermischung kann mechanisch mittels eines Rührers oder einer Rührschnecke oder Gegenstromvermischung bei Hochdruckverarbeitung durchgeführt werden. Die Reaktionstemperatur, d.h. die Temperatur, bei die Umsetzung erfolgt, beträgt üblicherweise > 20 °C, bevorzugt 50 bis 150 °C.

Die Polyisocyanat-Polyadditionsprodukte (ii) der erfindungsgmemäß hergestellten Verbundelemente weisen bevorzugt ein Elastizitätsmodul von >275 MPa im Temperaturbereich von −45 bis +50°C (nach DIN 53457), eine Adhäsion zu (i) und (iii) von >4 MPa (nach DIN 53530), eine Dehnung von >30% im Temperaturbereich von −45 bis +50 °C (nach DIN 53504), eine Zugfestigkeit von >20 MPa (nach DIN 53504) und eine Druckfestigkeit von > 20 MPa (nach DIN 53421) auf.

Die nach dem erfindungsgemäßen Verfahren herstellbaren Verbundelemente weisen folgende Vorteile gegenüber bekannten Konstruktionen auf:

- Streben und ähnliche Versteifungselemente werden fast vollständig überflüssig. Dies führt zu einer erheblichen Kostenreduktion in der Produktion durch Materialersparnis und einen wesentlich einfacheren Korrosionsschutz.

- Bei einem Einsatz im Schiffbau ergeben sich durch das geringere Gewicht eine höhere Tonnage bzw. ein geringerer Treibstoffverbrauch.

- Die Wartung beispielsweise hinsichtlich Korrosionsschutz wird wesentlich vereinfacht. Dadurch ergeben sich längere Instandsetzungsintervalle.

- Die Sandwichstruktur mit dem Polyisocyanat-Polyadditionsprodukt, beispielsweise dem Polyurethanelastomer, führt zu einer besseren Energieabsorbtion und damit geringeren Rißfortpflanzung. Bekannte Stahlkonstruktionen neigen nach einer Perforierung bei weiterer Belastung stark zu einer Rißbildung, d.h. die Leckage breitet sich großflächig über den Schiffsrumpf aus. Dadurch ergibt sich eine Minimierung des Schadensrisikos im Falle von Unfällen oder extremen Be-

lastungen. Dieser verbesserte Sicherheitsstandard ist insbesondere für Tankschiffe vorteilhaft.

- Die Polyisocyanat-Polyadditionsprodukte auf der Basis von Polyetherpolyalkoholen sind stabiler gegen einen hydrolytischen Abbau als Produkte auf der Basis von Polyesterpolyalkoholen. Dies bietet insbesondere für einen Einsatz der Verbundelemente im Schiffbau erhebliche Vorteile.
- Die Reaktionsmischung enthaltend die Polyetherpolyalkohole zur Herstellung von (ii) weist eine deutlich niedrigere Viskosität als Reaktionsmischungen auf der Basis von Polyesterpolyalkoholen auf. Dadurch ist eine einfachere und schnellere Fertigung der Verbundelemente möglich.

- Der bevorzugte Gehalt an Füllstoffen in den bevorzugten Polyisocyanat-Polyadditionsprodukten bewirkt eine Verringerung des thermischen Ausdehnungskoeffizienten von (ii) und damit eine Angleichung an die Koeffizienten von (i) und (iii). Spannungen zwischen (i), (ii) und (iii) durch eine thermischen Belastung insbesondere durch die Umgebungstemperatur, beispielsweise im Falle von Schiffsrümpfen durch unterschiedliche Wassertemperaturen, konnten erfindungsgemäß verringert werden. Die Haftung von (ii) an (i) und (iii) wurde dadurch nachhaltig verbessert.

- Durch das bevorzugte Bestrahlen der Oberflächen von (i) und (iii) Sand konnte die Haftung von (ii) an (i) und (iii) deutlich verbessert werden. Durch die verbesserte Haftung werden stabilere und haltbarere Konstruktionselemente zugänglich.

Entsprechend finden die erfindungsgemäß erhältlichen Verbundelemente Verwendung vor allem in Bereichen, in denen Konstruktionselemente benötigt werden, die großen Kräften standhalten, beispielsweise als Konstruktionsteile im Schiffbau, z.B. in Schiffsrümpfen, beispielsweise Schiffsdoppelrumpfe mit einer äußeren und einer inneren Wand, und Laderaumabdeckungen, oder in Bauwerken, beispielsweise Brücken oder als Konstruktionselemente im Hausbau, insbesondere in Hochhäusern.

Die erfindungsgemäßen Verbundelemente sind nicht mit klassischen Sandwichelementen zu verwechseln, die als Kern einen Polyurethan- und/oder Polyisocyanurathartschaumstoff enthalten und üblicherweise zur thermischen Isolierung eingesetzt werden. Derartige bekannte Sandwichelemente wären aufgrund ihrer vergleichsweise geringeren mechanischen Belastbarkeit nicht für die genannten Anwendungsbereiche geeignet.

Patentansprüche

1. Verbundelemente, die folgende Schichtstruktur aufweisen:

(i) 2 bis 20 mm Metall,

(ii) 10 bis 100 mm kompakte Polyisocyanat-Polyadditionsprodukte erhältlich durch Umsetzung von (a) Isocyanaten mit (b) Polyetherpolyalkoholen gegebenenfalls in Gegenwart von (c) Katalysatoren und/oder (d) Hilfs- und/oder Zusatzstoffen,

(iii) 2 bis 20 mm Metall.

2. Verbundelemente nach Anspruch 1, dadurch gekennzeichnet, daß man als (b) eine Mischung einsetzt, die enthält:

(b1) 40 bis 99 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 1,5 bis 2,99 und einem mittleren Molekulargewicht von 400 bis 8000 und

(b2) 1 bis 60 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 3 bis 5 und einem mittleren Molekulargewicht von 150 bis 8000.

3. Verbundelemente nach Anspruch 2, dadurch gekennzeichnet, daß man als (b) eine Mischung einsetzt, die enthält:

(b1) 40 bis 98 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 1,5 bis 2,99 und einem mittleren Molekulargewicht von 400 bis 8000,

(b2) 1 bis 60 Gew.-% Polyetherpolyalkohol mit einer mittleren Funktionalität von 3 bis 5 und einem mittleren Molekulargewicht von 150 bis 8000 und

(b3) 1 bis 50 Gew.-% mindestens einer gegenüber Isocyanaten reaktiven Verbindung, die ein Kohlenwasserstoffgerüst mit 10 bis 40 Kohlenstoffatomen und 2 bis 4 gegenüber Isocyanaten reaktive Gruppen aufweist.

4. Verbundelemente nach Anspruch 1, dadurch gekennzeichnet, daß (ii) 10 bis 70 Gew.-% Füllstoffe, bezogen auf das Gewicht von (ii), als (d) Hilfs- und/oder Zusatzstoffe enthält.

5. Verbundelemente nach Anspruch 1, dadurch gekennzeichnet, daß (ii) ein Elastizitätsmodul von >275 MPa im Temperaturbereich von -45 bis +50 °C, eine Adhäsion zu (i) und (iii) von >4 MPa, eine Dehnung von >30% im Temperaturbereich von -45 bis +50 °C, eine Zugfestigkeit von >20 MPa und eine Druckfestigkeit von > 20 MPa aufweist.

6. Verfahren zur Herstellung von Verbundelementen nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß man zwischen (i) und (iii) durch Umsetzung von (a) Isocyanaten mit (b) Polyetherpolyalkoholen gegebenenfalls in Gegenwart von (c) Katalysatoren und/oder (d) Hilfs- und/oder Zusatzstoffen kompakte Polyisocyanat-Polyadditionsprodukte herstellt, die an (i) und (iii) haften.

7. Verbundelemente erhältlich durch ein Verfahren gemäß Anspruch 6.

8. Verbundelemente nach Anspruch 7, die die Eigenschaften gemäß Anspruch 5 aufweisen.

9. Verwendung von Verbundelementen nach einem der Ansprüche 1 bis 5, 7 oder 8 als Konstruktionsteile im Schiffbau, beispielsweise in Schiffsrümpfen und Laderaumabdeckungen, oder in Bauwerken, beispielsweise Brücken.

10. Schiffe oder Brücken enthaltend Verbundelemente nach einem der Ansprüche 1 bis 5, 7 oder 8.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03545

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B17/08 C08G18/48 B63B3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G B32B B63B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 21029 A (KENNEDY STEPHEN J ;FERN INVESTMENTS LIMITED (CA)) 22 May 1998 (1998-05-22) page 12, line 20 - page 19, line 14 claims 1,3 ---	1,5-10
A	EP 0 405 300 A (CHISSO CORP) 2 January 1991 (1991-01-02) page 2, line 42 - page 3, line 25 example 1 ---	1
A	US 4 859 523 A (ENDOH HIROSHI ET AL) 22 August 1989 (1989-08-22) column 7, line 41 - column 8, line 64 claims 1,9 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 September 1999	16/09/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Neugebauer, U

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/03545

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9443 Derwent Publications Ltd., London, GB; Class A25, AN 94-347175 XP002113984 & JP 06 271639 A (INOAC CORP KK), 27 September 1994 (1994-09-27) abstract	1,2,4,6, 7,9
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Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 99/03545

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 6 B32B17/08 C08G18/48 B63B3/00

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 6 C08G B32B B63B

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie*	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	WO 98 21029 A (KENNEDY STEPHEN J ;FERN INVESTMENTS LIMITED (CA)) 22. Mai 1998 (1998-05-22) Seite 12, Zeile 20 - Seite 19, Zeile 14 Ansprüche 1,3 ---	1,5-10
A	EP 0 405 300 A (CHISSO CORP) 2. Januar 1991 (1991-01-02) Seite 2, Zeile 42 - Seite 3, Zeile 25 Beispiel 1 ---	1
A	US 4 859 523 A (ENDOH HIROSHI ET AL) 22. August 1989 (1989-08-22) Spalte 7, Zeile 41 - Spalte 8, Zeile 64 Ansprüche 1,9 --- -/--	1

[X] Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

[X] Siehe Anhang Patentfamilie

* Besondere Kategorien von angegebenen Veröffentlichungen :
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"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
1. September 1999	16/09/1999

Name und Postanschrift der Internationalen Recherchenbehörde	Bevollmächtigter Bediensteter
Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Neugebauer, U

Formblatt PCT/ISA/210 (Blatt 2) (Juli 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/03545

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		JP 60055020 A	29-03-1985

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 99/03545

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie°	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	DATABASE WPI Section Ch, Week 9443 Derwent Publications Ltd., London, GB; Class A25, AN 94-347175 XP002113984 & JP 06 271639 A (INOAC CORP KK), 27. September 1994 (1994-09-27) Zusammenfassung	1,2,4,6, 7,9
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(57) Abstract

A composite laminate panel suitable for building containment vessels, and in particular, suitable for building double hull oil tankers. The laminate has two facing metal layers structurally bonded to a polyurethane elastomer core. The laminate is used in various hull components, such as the hull plates, longitudinal girders, transverse frames and bulkheads. The laminate is used to build the inner hull and outer hull, and may be used to build the structural supports between the inner and outer hulls. The innermost layer of inner hull contains the ship's cargo. The elastomer core of the inner hull laminate isolates the innermost hull skin from cracks, thereby preventing a loss of cargo such as oil into the environment, when the outer hull is pierced, penetrated or ruptured in an accident or grounding.

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COMPOSITE STEEL STRUCTURAL PLASTIC SANDWICH PLATE SYSTEMS

FIELD OF THE INVENTION

The present invention relates to a flexible impact and tear resistant composite sandwich plate and construction system for vessels such as tankers, bulk carriers or ships for which it is desirable to contain the vessel contents during conditions of extreme or accidental load.

DESCRIPTION OF THE PRIOR ART

Increased social, economic and political pressure has led to the development of technology to reduce or eliminate the risks of pollution and resulting damage to the marine environment, as well as the loss of valuable cargo, that may result from cargo leaking due to rupture of a vessel under extreme or accidental loads such as collisions, grounding, fire and explosion. In particular, vessels carrying hazardous materials are increasingly subject to additional requirements imposed by regulatory agencies, ship and cargo insurers, and ship owners and financiers. The high cost of hazardous spill liability and increasing cargo values has further encouraged the development of leak and rupture resistant vessels.

One approach to containing vessel contents is the provision of double hulls for oil tankers. An inner cargo containing hull of a stiffened single plate construction is supported within an outer protective hull, which is also a stiffened single plate construction. A conventional double hull has longitudinal and transverse frames between the inner and outer hulls. A more advanced, alternative double hull has only longitudinal frames between the inner and outer hulls, allowing for simplified construction suitable for assembly line production by robotic devices. Both conventional and advanced double hull designs have transverse bulkheads between cargo compartments in the inner

hull, and may have bulkheads between ballast compartments which are generally located between the inner and outer hulls. Variations in double hull design include constructions with a double bottom only, or with a double bottom and double hull sides. To reduce weight, the deck is generally a single plate construction. Alternatively, convexly curved hull plates between longitudinal frames may provide high energy absorption in the curved plate double hull.

Fig. 1 shows a cross-section of a typical double hull oil tanker designed according to conventional naval architecture. Fig. 2 illustrates the arrangement of cargo tanks and other sections for a typical double hull vessel.

The advantages of double hull construction over conventional single hull designs are also well known. These advantages include improved cargo handling efficiency, better cargo purity, and reduced water pollution by isolating ballast tanks from cargo holds. Furthermore, double hulls constructed to international standards which require a two meter space between inner and outer hulls also offer reduced risk of leakage or rupture due to penetration of the outer hull during collisions or groundings. The claimed innovative features of advanced double hulls are improved strength, ease of manufacture and reduced welding and steel surface areas in ballast tanks, increased accessibility to ballast tanks which results in better inspection and improved maintenance and inner hull retention of oil during high energy grounding. With current technology, double hull vessels involved in low energy, low velocity impacts are less likely to be compromised and less likely to cause pollution than a single hull vessel. The improved tanker designs, such as double-bottom, double sides, double hull, mid-deck, etc. are known to reduce but not eliminate the risk of oil spills in accidents. Although tests indicate that an advanced all steel double hull design will dissipate more energy than a conventional all steel double hull design, both designs are subject to compromise of the inner hull due to crack propagation resulting from

fatigue cracks or from cracks that propagate from a ruptured plate during extreme load events.

Patents related to improving the energy absorption capacity of double hull construction due to accidental or extreme load events such as grounding or collision include U.S. Patent Nos. 5,218,919 to Krulikowski III et al. and 5,477,797 to Stuart. Both patents are directed to retrofitting existing single hull tankers with external hulls to make a double hull tanker. Krulikowski III et al. describe the use of energy absorbing telescoping members arranged in a truss-like formation to support a laminated steel auxiliary hull to the outside of an existing oil tanker hull. Construction details of attachments to transverse bulkheads and deflection control devices are also described. The void between hulls is filled with polyurethane foam/balls to distribute impact forces, to support the auxiliary hull under hydrostatic loads and to provide additional buoyancy in the case where the auxiliary hull is ruptured. Stuart describes the construction of an auxiliary hull attached to the outside hull of an existing oil tanker. It is composed of a series of longitudinally framed steel plates that form a honeycomb configuration, when viewed in section, between the hulls. The combination of stress relief joints, which make the outer hull discontinuous, and the honeycomb inner hull structure create a damage resistant hull. The construction also allows the inner hull space to be flooded to any level to provide the appropriate ballast by means of a pressurized inert gas and a vacuum pressure system. These retrofitted external hull structures fail to address the possibility of crack propagation into the inner hull due to rupture of the outer hull, and inadequately address the cost and practicality of fabrication and maintenance of the auxiliary hull structure. In current retrofit designs, access between the hulls for inspection and corrosion maintenance is difficult, if not impossible. The external hull in a retrofit design generally does not participate in carrying all of the operational loads, and adds significant dead weight to the

tanker with limited structural functionality.

U.S. Patent Nos. 4,083,318 to Verolme and 4,672,906 to Asai are directed to LNG (liquid natural gas) tankers and to tankers carrying cryogenic or high temperature freight in which the cargo tanks are separate structures from the tanker and do not form part of the load carrying hull girder system of the tanker.

Current all steel double hull construction has serious disadvantages which lower the likelihood that these design types will meet the performance criteria of zero oil outflow after accidental or extreme load events such as collisions, groundings, explosions or fire, and remain competitive relative to construction, maintenance and service life costs. One disadvantage is that current double hull construction is based on traditional naval architecture design concepts in conjunction with international agreements and national standards that stipulate the use of double hull construction with a minimum separation between hulls which is related to statistical data of measured rock penetrations from recorded tanker casualties.

Hulls constructed according to traditional naval architecture standards generally provide a complex system of steel plates and plate steel structural members, such as frames, bulkheads and girders. The carrying capacity of the steel plates and supporting members is increased by reinforcing the plates and structural members with multiple stiffeners of the type well known in the art, such as flat, angle or channel metal stock fastened to plate surfaces. This complex hull structure and plate stiffener system is a source of fatigue failures and a source for tearing (rupture) of the hull plate during accidental or extreme loads. This type of hull is costly to fabricate due to the large number of pieces which must be cut, handled and welded, and because of the significantly increased surface area on which protective coatings must be applied. Also, these typical complex structural systems are very congested, leading to poor access, poor inspection, poor and costly maintenance, and a decreased service life due to corrosion.

Recent large scale grounding tests on double hull sections also indicate that despite the superiority of double hull vessels over single hull vessels, rupture of the interior hull of currently available steel double hull designs may occur as a result of crack propagation from the initial rupture of the outside hull primarily at or near transverse structural members. The crack initiated in the outside hull propagates through the structural members between the inner and outer hulls and is transmitted to the inner hull. The obvious consequence of inner hull rupture will be oil outflow from each ruptured cargo hold. Providing a crack arrest layer or other structure to prevent the propagation of cracks through the steel structure into cargo tanks is not disclosed in current design alternatives. Therefore, preventing or reducing oil outflow in the event of accidental or extreme load events is not adequately addressed by currently available design alternatives.

A large scale composite steel polyurethane foam sandwich plate has been tested for its ability to prevent leak and rupture of a hull. These tests illustrate that polyurethane foam does not adequately adhere to the steel plates and has little shear strength. Low shear strength minimizes the flexural capacity of the composite and lack of adhesion precludes the possibility of using polyurethane foam and steel in a composite to increase the in-plane buckling capacity so that plate stiffeners can be eliminated. The low density foam used in the test composite had little or no tensile strength and insufficient compressive strength to be beneficial structurally. Generally, the tested foam acted as a crack arrest layer but did not function structurally. Therefore, the desired crack arresting structural composite configuration was not achieved. The tested foam possessed some energy absorption capacity; however, this capacity was small when compared to that of the steel in membrane action. The foam lessens the localized straining of the steel plates around a concentrated load point which delays, but does not prevent, the shear tension failure of the steel hull plates.

Thus, a need exists in the art for a hull construction system that simplifies the complexity of hull structure, reduces fabrication and maintenance costs, and increases energy absorption capacity and plastic behavior in the event of accidental or extreme loads to reduce or eliminate cargo loss due to hull rupture and crack propagation.

SUMMARY OF THE INVENTION

The above-described drawbacks inherent in the art for providing double hull tankers are advantageously eliminated in accordance with the teachings of the present invention by bonding a tough structural elastomer between steel plates to form steel-elastomer-steel composite hull panels, frames and supporting members. The elastomer is preferably hydrophobic to prevent water absorption which could lead to rusting of the plates and should have sufficient ductility to exceed the yield strain of the steel plates without rupturing. The composite panels are used in constructing at least the inner hull of the double hull. Preferably the steel-elastomer-steel composite panels are used to construct the inner hull, outer hull, bulkheads, floors, decks and collapsible frame and support members and may be formed in any necessary shape. The elastomer layer within the composite panels forming the inner hull particularly provides an effective crack arrest layer between the inner steel plate of the inner hull and the outer steel plate of the inner hull, which effectively isolates the inner steel plate of the inner hull from cracks that propagate from the outer hull, the transverse members, such as floor frames and bulkheads, and other supporting elements, such as web frames and horizontal frames, that are designed for both in-service loads and for accidental or extreme loads. Furthermore, because the composite panels are stronger and stiffer than conventional steel plates, the number of framing and supporting elements can be significantly reduced while meeting or exceeding current design standards for strength, service life, construction

cost, maintenance cost and survivability.

In accordance with the teachings of the present invention, a composite steel polyurethane elastomer sandwich plate system with properly detailed floor and transverse bulkheads and which is particularly suited for use in containment vessels such as, for example, oil tankers, is fabricated to substantially eliminate the drawbacks associated with known all steel vessels. The specific details relating to ship design may be found in American Bureau of Shipping and Affiliated Companies, 1996 Part 3, Hull Construction and Equipment; Part 5, Specialized Vessels and Services, which is incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

The teachings of the present invention can be readily understood by considering the following detailed description in conjunction with the accompanying drawing in which:

FIG. 1 is a perspective cross-sectional view of a prior art all-steel double hull oil tanker which includes a unidirectional girder system and stiffened steel hull plates;

FIG. 2 is a plan view of a prior art double hull tanker illustrating the general arrangement of cargo and ballast compartments;

FIG. 3 is a cross-sectional view of a prior art double hull tanker midsection taken at a transverse bulkhead illustrating the structural members and stiffener system;

FIG. 4 is a cross-sectional view of a double hull midsection taken at a transverse bulkhead constructed with composite panels according to the present invention;

FIG. 5 is a partial cross-section view of a cargo hold of a double hull vessel constructed with composite panels according to the present invention;

FIG. 6 is a cutaway cross-section view of a double hull vessel transverse bulkhead construction with composite panels according to the present invention;

FIG. 7 is a cutaway cross section view of a crack

arrest detail for a transverse bulkhead according to the present invention;

FIG. 8 is a cross-section view of a composite panel constructed according to the present invention;

FIG. 9 is a cross-section view of the inner hull and bulkhead constructed with composite panels according to the present invention;

FIG. 10 is a cross-section view of the inner and outer hull and supporting members constructed with composite panels according to the present invention;

FIG. 11 is a cross-section view taken along line 11-11 in Fig. 10, showing details of the elastomer plug sealing the crack arrest cut-out;

FIG. 12 is a cross-section view of a composite panel under construction according to the present invention; and

FIG. 13 is a cross-section view of the inner hull, bulkhead and composite spacer constructed with composite panels according to the present invention.

DETAILED DESCRIPTION

The teachings of the present invention are applicable to any structure, vessel, tanker, bulk carrier or ship in which it is desired to contain the contents during an extreme or accidental load event. For the sake of illustration only, the present invention will be discussed in the context of double hull oil tankers. Those skilled in the art will readily appreciate how the teachings of the present invention can be incorporated into the structural configuration of other vessels, bulk carriers, etc., such as, road vehicles, rail cars and storage tanks.

In existing designs, research, rules and regulations and construction for impact resistance and survivability have generally been directed to all-steel conventional double hulls and advanced double hulls, also known as unidirectional stiffened girder double hulls. A typical conventional double hull (CDH) design as illustrated in Figs. 2 and 3, for example, for a 40,000 DWT (deadweight

tons) tanker is characterized by an inner hull 10 and an outer hull 12, with an orthogonally stiffened bottom 1, transverse web frames 2 and longitudinal girders 3. Hull plates 4 are welded or otherwise attached to the longitudinal girders 3. Web frames 2, oriented transversely to the longitudinal girders 3, are attached between longitudinal girders 3 to retain and stabilize the girders 3. The plan view of FIG. 2 illustrates a typical layout for a tanker having an outer hull 12 and an inner hull 10 in the cargo containing portion of outer hull 12. The compartmentalized cargo holds 13 in the inner hull 10 are separated by bulkheads 6. Compartments 102, outboard from the cargo holds 13, may serve as ballast tanks in the lower part of the hull.

Typically, the load carrying capacity of the hull and deck plates 4 and 5, respectively, and the web and floor frames 2 and 11, respectively, bulkheads 6 and girders 3 are increased by the addition of stiffeners 7, as shown in FIG. 3. Numerous stiffeners 7 are required to strengthen hull plates 4 of both the inner and outer hulls 10, 12 and deck plates 5. Additional stiffeners, not shown, are also found on girders 3, bulkheads 6, frames 2 and girders 3. It is recognized that this type of construction may not be designed to be impact resistant for accidental or extreme load events such as groundings and collisions. An advanced double hull (ADH) system has primarily longitudinal unidirectional framing between outer and inner hulls. The advanced double hull has significantly fewer transverse members, but the advanced double hull does have transverse bulkheads 6 between cargo compartments 13, and may have transverse floor frames 11 between ballast compartments 102 located between the inner and outer hulls. Like conventional double hulls, the carrying capacity of advanced double hull steel plate components is enhanced by fixing numerous stiffeners 7 to the surface of the plate steel components.

Recent studies of the effect of high energy impact grounding on both conventional and advanced all steel double

hull construction systems demonstrates that the outer hull 12 will generally rupture longitudinally as a result of exceeding the maximum strain in membrane action of the steel plate 9 between longitudinal girders 3, and that rupture of the inner hull 10 is initiated by vertical crack propagation from transverse frames 2, 11 and bulkheads 6. This in turn is initiated by the rupture of the outer hull 12 at or near transverse members 2, 6, 11, such as, bulkheads 6, floors 11 or frames 2. On the intrusion of a foreign object into the vessel's hull, a portion of the inner hull 10 is pushed inward ("lifted") either by direct contact with the intruding object, or indirectly by support members, such as, for example, a hull girder 3, or floor frame 11 which is pushed inward by the intruding object. The inner hull plates 14 in the impact area may deform as a membrane until a transverse member 11 restrains the inner hull 10 from further inward movement, e.g., "lift" of the inner hull plate 14 is restrained, causing extreme membrane stresses at or near the location of the intruding object. The extreme membrane stress triggers an initial crack, either in the transverse member 2, 6, 11 restraining the inner hull plate 14, or directly in the restrained inner hull plate 14, leading to inner hull 10 rupture. It is generally required that a spill proof tanker bottom structure must be designed to allow "lift" and inelastic membrane deformation of the inner hull 10 without rupture.

To achieve this purpose, in accordance with the present invention, a crack arrest layer 15 (FIG. 4) is incorporated in the hull structure at least at or near all transverse members, such as for example floor frames 24 and bulkheads 26, but preferably throughout the entire hull structure, wherever practical.

In the discussions herein for purposes of orientation, when "inner" is used with respect to components, it will generally refer to components relatively closer to the cargo hold of the vessel. When "inner" is used with respect to a surface, it will generally refer to a surface facing the cargo hold. In particular, the inner

surface 63 (FIG. 8) of the inner metal plate or layer 34 of the inner hull 20 faces and is generally exposed to the cargo hold 68. When "outer" is used with respect to components, it will generally refer to components relatively further from the cargo hold. When "outer" is used with respect to a surface, it will generally refer to a surface facing away from the cargo hold.

Referring now to FIG. 4 which illustrates the present invention, a composite panel vessel construction system for building, for example, a tanker constructed with a unidirectional double hull sandwich plate system (UDHSPS), incorporates a tough impact resistant hull 16 composed of steel-elastomer-steel composite panels 18 supported by a properly detailed collapsible structure, some or all of which may also be of composite panel construction. Referring now to Figure 5, the composite panels 18 are comprised of an inner metal plate 34 spaced apart from and facing an outer metal plate 36, the inner and outer metal plates being bonded to an intermediate elastomer core 38. An inner hull having two opposite sides 74 and 78, and a bottom 76, forms a cargo hold 68. A deck 40 extends from the top of side 74 to the top of side 78 to close the top of the cargo hold 68. A bulkhead 26 at each end of the cargo hold 68 is connected to the sides 74 and 78, and the bottom 76 and deck 40, to substantially completely enclose cargo hold 68. An outer hull 28 having two sides 80 and 82 and a bottom 84, is spaced apart from and encloses, respectively, the two sides 74 and 78 and bottom 76 of inner hull 20. The outer hull 28 is connected to the inner hull 20 by support members including longitudinal girders 22 and transverse floor frames 24. At least the inner hull 20 is constructed of composite panels 18. Preferably, the inner hull 20, outer hull 28, longitudinal girders 22, floor frames 24 and bulkheads 26 are constructed of composite panels 18. The various components, whether made of composite panels 18 or of conventional single plate steel are connected together by welding or by other conventional means, with certain allowances, discussed below, necessary to accommodate the

elastomer core 38 of the composite panel 18.

The UDHSPS will significantly enhance survivability of the inner cargo containing hull 20 in the event of a collision or grounding, and significantly reduces, if not eliminates, the outflow of oil during such an event, particularly in comparison to conventional double hull counterparts. The UDHSPS is constructed to behave in a ductile mode under accidental or extreme loads and to absorb the energy through inelastic membrane action of the composite panel hull and plastic deformation of conventional steel and/or steel-elastomer-steel composite panel supporting elements. To minimize or eliminate oil outflow, cargo hold crack or tear propagation is prevented. To prevent tearing or cracking as a mode of failure during extreme load events, absorption and dissipation of the impact energy is maximized by engaging as much of the ship as possible in the collision or grounding. In doing so, the consequence of oil outflow is minimized, if not eliminated altogether.

Insofar as oil tankers are concerned, the UDHSPS can be designed to provide equivalent or greater strength for operational loads than existing conventional or advanced all- steel double hull vessels designed according to current standards. As shown in cross-sectional detail in FIG. 5, the steel-elastomer-steel hull girder 22 according to the present invention has an inner metal plate 34 and an outer metal plate 36 on an elastomer core 38 to provide sufficient bending, shear and torsional strength to act as a hollow thin-walled box beam capable of withstanding typical or extreme static and dynamic loads such as those associated with operating a cargo vessel. These loads include for example, still water loads, dry docking loads, thermal loads, wave-induced dynamic pressure distributions on the hull, sloshing of liquid cargoes, green-seas on the deck, wave slap, inertia loads, launching and berthing loads, ice breaking loads, slamming, forced vibration, collision and grounding. FIGS. 4 and 6 illustrate a double hull midship section 42 and transverse bulkhead 26 for a double

hull tanker constructed with composite steel-elastomer-steel panels 18. Both the inner and outer hulls 20 and 28, respectively, are constructed from composite steel-elastomer-steel panels 18 suitably designed and dimensioned for a vessel of a particular size and purpose. The transverse bulkheads 26 shown in Figs. 6, 7 and 9 are also constructed of composite steel-elastomer-steel panels 18 supported by both horizontal and vertical web plates 30 and 32 respectively, which may also be of composite panel 18 construction.

The composite panels 18 can be manufactured as individual components, such as, for example, hull panels 17, floor frames 24, girders 22, bulkheads 26, etc., which can subsequently be shipped or assembled into sub-assemblies of a complete vessel, in a number of different ways. The inner and outer metal plates 34 and 36 (FIG. 5) of a composite panel 18 are positioned in an appropriate spaced apart relationship to form a cavity 56 (FIG. 12) for the elastomer core 38. In the preferred embodiment, the inner and outer metal plates 34 and 36 respectively, are steel. Other suitable metals may be used, such as for example, stainless steel for high corrosion applications, or aluminum for light weight applications. Because the composite panels 18 are significantly stronger than single plate metal, other softer types of metal may be used to construct composite panels.

As shown in FIG. 8, preferably the appropriate spacing between the inner and outer metal layers 34 and 36 is maintained by spacer elements 44 ("spacers") provided between the inner and outer metal layers 34 and 36. The spacer element 44 may comprise a continuous strip-like member, or alternatively the spacer element 44 can comprise multiple individual spacer members arranged randomly or in a pattern. The spacers 44 can be made of metal or any other suitable material that is placed between the metal inner and outer layers 34 and 36. The spacer elements 44 may be welded or bonded to the inner and/or outer metal layer 34 and 36. Preferably, the spacers 44 are continuous strip-like members having opposite longitudinal edges 46 and 50.

The spacers 44 are welded on one longitudinal edge 46 with fillet welds 48 to the outer metal plate 36 at points along the mid-line of the plate 36 and generally mid-way between longitudinal girders 22. Preferably the spacers run generally only in the longitudinal direction with respect to the hull construction, but may also run in a transverse direction where necessary. The inner metal plates 34 which have substantially the same length and width dimensions as the outer metal plates 36, are laterally staggered, so that the edges 52 and 54 of the abutting inner plates 18a and 18b fall naturally on the spacer edge 50. The edge 50 of the spacer 44 may serve as a support for adjacent edges 52 and 54 of abutting panels 18a and 18b. The spacer element edge 50 acts as a weld backing bar, supporting the inner metal layer plates 18a and 18b until butt weld 55 is completed. The spacer element 44 acting as a backing bar also helps to establish a proper weld gap and minimizes weld preparation. The butt weld 55 securely fastens the edges 52 and 54 of panels 18a and 18b to the edge 50 of spacer 44. The elastomer core 38 may be added subsequent to welding of the plates 18a and 18b through apertures 70 in the inner or outer metal plates 34 and 36, respectively.

The spacer elements 44 may alternatively be premanufactured or precast elastomer strips or blocks, bonded or thermoset into position between the metal layers 34 and 36. Alternatively, the spacing may be maintained by, for example, a manufacturing jig which holds the inner and outer plate, 34 and 36 respectively, in a spaced apart relationship to form core cavity 56 until the elastomer core 38 is provided and cured.

Preferably, the individual components, such as the longitudinal girders 22, floor frames 24, bulkheads 26, inner and outer hull 20 and 28 and composite hull panels 18 are integrally manufactured on a vessel under construction by at least partially fastening the inner and outer steel plates 34 and 36 of a particular component at the designated location for that component, while maintaining a suitable core cavity 56 between the plates of the component. The

elastomer is subsequently placed in the core cavity between the inner and outer metal plates 34 and 36 by flowing or injecting it in a liquid or viscous state, and allowing or causing the elastomer to cast in place in the core cavity. The elastomer can alternatively be placed in the core through a tube or tubes cross-sectionally dimensioned to enter the empty core cavity at an open or unfastened edge of the component, the tubes being of a length suitable to enter the dimensions of the component. As elastomer enters through the tubes into the cavity to fill the void between the plates, the tubes are withdrawn. The elastomer takes on the form of the void, in this case the core cavity 56, in which it is cast. Alternatively, the elastomer can be placed in the core cavity by injection or flowing through plate apertures or ports 70 (FIG. 7) provided in the inner or outer metal plates 34 and 36. The preferred location of the plate apertures 70 are on the inner metal plate 34 of the outer hull 28 and the outer metal plate 36 of the inner hull 20, away from exposure to the outside environment and away from exposure to the cargo. These plate apertures 70 are then sealed with threaded metal plugs 72. The elastomer can be placed in the core cavity 56 of individual construction components as construction of the hull progresses, or large sections or an entire hull can be constructed with an empty core cavity 56 between inner and outer plates 34 and 36, and elastomer can subsequently be placed in the core cavity 56. Once the flowable elastomer is in the core cavity 56, the elastomer core 38 is cured by, for example, applying heat.

The preferred thickness of each of the inner and outer steel layers 34 and 36 ranges from, for example, 6mm to 25mm, with 10mm considered an ideal thickness. These dimensions will change with service or component requirements, and with changes in the type or quality of the materials employed. It will be appreciated by those familiar with the art that the inner and outer metal layers 34 and 36 need not have identical thickness dimensions and need not be made of the same type or quality of metal.

Numerous combinations and variations are possible without deviating from the spirit or scope of the invention.

The dimensional thickness of the composite panel can be selectively adjusted during assembly of the laminate to achieve desired structural strength requirements for various components and applications. The dimensional thickness of each of the inner and outer metal plates 34 and 36 and/or the elastomer core 38 can be varied according to a particular requirement. Furthermore, the laminate panels 18 can be constructed to have dimensionally thickened panel portions for localized adjustment of structural strength. The dimensionally thickened portion of a panel can be the result of a thickened elastomer core 38 provided by varying spacer element 44 dimensions such as, by varying the depth of the spacer element along the length of the spacer element, providing composite panels 18 with variable thickness. Alternatively, the dimensionally thickened panel can result from thickening of one or both of the metal inner and outer plates 34 and 36 of the composite.

The elastomer is preferably a thermosetting type of plastic, which may require heat to cure the material and complete the casting process. The preferred polyurethane elastomers cure at temperatures of approximately 20°C-60°C. Residual heat from the welding of components will provide a portion of the casting heat, particularly near the weld joints. However, portions of the core cavity 56 that are remote from the weld joints will require application of supplemental curing heat. The heat necessary to cure the elastomer core 38 can be provided to the inner and outer metal plates 34 and 36 of the composite panel 18. The metal plates 34 and 36 will readily transmit the heat to the elastomer 38 in the core cavity 56 to complete casting of the elastomer. Alternatively, an elastomer can be selected that flows at reduced or elevated temperatures, and cures at ambient temperatures.

After the core cavity 56 is filled with elastomer 38, any apertures 70 in the inner and outer metal plates 34 and 36 are sealed with threaded metal plugs 72. The

apertures 70 are preferably on the inner plate 34 of the outer hull 28, away from exposure to the outside environment, and on the outer plate 36 of the inner hull 20, away from exposure to the cargo. Thus, the apertures 70 and plugs 72 are generally exposed to the void between the inner hull 20 and outer hull 28, where inspection and maintenance is readily possible.

The component assembly process is repeated to complete installation of adjoining components as the vessel construction progresses. The assembly methods discussed herein are merely illustrative. Other methods of vessel assembly are known and are contemplated as being part of the present invention.

Because structural or adhesive characteristics of a selected elastomer may be damaged by the heat of welding, where adjacent composite components 18a and 18b are fastened by welding after the elastomer 38 is in place between the inner and outer plates, 34 and 36, a welding margin 58 must be provided. The welding margin 58 is a suitably dimensioned portion of the core cavity 56 proximal to a joint to be welded, which margin 58 is at least initially devoid of elastomer. A margin 58 of approximately 75 mm from the joint being welded is sufficient to prevent damage to the elastomer core 38. Steel temperatures 75 mm from a weld joint are generally about 150°C while the temperature of the steel at or close to the weld joint is significantly higher. After completion of the welding operation, and after the joint has cooled sufficiently, for example, to 150°C, the void in the welding margin can be filled through apertures 70 provided for that purpose in the component inner and outer metal plates 34 and 36. Alternatively, the welding margin 58 of one component can be filled through the empty core cavity 56 of an adjacent component.

It is contemplated that an elastomer will be selected with bonding capabilities suitable for the metal of the inner and outer metal plates 34 and 36. Alternatively, suitable bonding agents can be used to promote adhesion, or adhesive can be used to bond the elastomer to the metal

plates. The metal "skin" plates can also, by known means, be mechanically or chemically bonded to a pre-cast elastomer core. Spacers of an appropriate dimension may be placed between the "skin" plates to maintain the proper spacing during bonding operations.

Although a variety of materials are suitable and contemplated for the core of the steel-elastomer-steel composite panel, the preferred elastomer for the core of the composite panel is a thermoset polyurethane elastomer having appropriate chemical and physical properties. Specific details relating to elastomers may be found in Engineered Materials Handbook, Volume 2, Engineering Plastics (1988 ASM International) which is incorporated herein by reference. Thermoset polyurethane elastomer is an engineered material with, for example, the following range of physical properties and characteristics: tensile strength of 20 to 55 MPa, shore hardness of 70A to 80D, elongation of 100-800%, flexural modulus of 2 to 104 MPa, glass transition temperature of -70 to 15°C, abrasion resistance, low-temperature flexibility, low-temperature impact strength, long-term flexibility, tear/cut resistance, fuel and oil resistance, good elasticity and rebound, ozone resistance, weather resistance and temperature resistance. These properties are defined and can be characterized in accordance with applicable ASTM standards. Commercial applications of polyurethane elastomers include load bearing industrial rollers, caster wheels, exterior painted autobody parts, hydraulic seals, drive belts, injection/blow-molded dust shields, injection molded grease boots (covers), blow and flat die extruded film and sheet products (0.03 mm to 3mm thick), tubing, hose covers, sport shoes, wire and cable protective covers. The properties and characteristics of commercially available polyurethane elastomers can be tailored for a particular application by varying the chemistry. Polyurethane elastomers have heretofore not been used in a composite sandwich with metal skins for containment vessels such as double hull oil tankers.

It is evident that the elastomeric core material

of a structural composite panel 18 must adhere securely to both metal skin plates 34 and 36 in order to support operational loads. Furthermore, the cured elastomeric core material 38 must possess suitable structural characteristics, such as sufficient density, tensile strength, ductility, shear strength and compressive strength to provide the composite panel 18 with the properties desirable in a ship building application, such as, for example, high strength and ductility, durability and impact resistance in accidental or extreme load events like groundings or collisions. A properly formulated polyurethane elastomer possesses other suitable characteristics, such as water and oil resistance, and thermal resistance for insulation.

The elastomer core 38 of the composite panel 18 construction contributes in carrying the operating loads in several ways. First, the adhesion developed between the steel inner and outer plates 34 and 36 and the elastomer 38 prevents local buckling of the relatively thin metal plates 34 and 36 that would occur under normal hogging and sagging moments and eliminates the need for closely spaced longitudinal stiffeners between the longitudinal girders 22 or the need for closely spaced longitudinal girders 22. Second, the elastomer core 38 is provided with physical properties and in dimensions suitable to transfer sufficient shear between the inner and outer metal plates 34 and 36 to enhance the flexural strength of the inner and outer plates 34 and 36. The inner and outer plates 34 and 36 of the composite panel 18, because of their separation, provide approximately ten times more flexural strength than that of conventional single metal plates 14 with the same total plate thickness. As a result of the significantly higher strength of a composite component when compared to a corresponding single plate component, composite components such as, for example, longitudinal girders 22, frames 24 or bulkheads 26, can be spaced further apart and thus fewer are required. Furthermore, the stronger composite components require significantly fewer or no stiffeners 7. Therefore,

without increasing the total weight of the steel required to build the vessel, steel normally used for the additional longitudinal girders 3, frames, 11 and 2, and plate stiffeners 7 required in prior art steel double hulls can be reallocated to the composite hull plates 17 and 18 and structural members such as girders 22, floors 24, bulkheads 26 and webs 32, to obtain stronger individual components capable of improved structural performance without increasing steel costs. The elastomer core 38 provides sufficient longitudinal shear transfer between the inner and outer metal plates 34 and 36 of the composite panel 18, to enable all of the plates 34 and 36 to contribute to the elastic section modulus and hence the moment resistance of the tanker as a whole. The elastomer increases the shear buckling capacity of the hull structure. By substituting the composite panel 18, constructed of two thinner steel plates 34 and 36 separated by and bonded to a structural elastomer 38, for the prior art single thicker steel plate, a tear or rupture resistant hull is achieved at a cost equivalent to or lower than conventional construction, since the steel plate may not have to be specified as a more costly notch tough steel. The distribution of the thickness of the two steel plates 34 and 36 in the composite panel 18 is not prescribed and can be distributed to optimize structural performance and durability for factors such as, for example, load bearing capacity, and corrosion and abrasion resistance.

The substitution of the composite panel 18 for conventional steel plate in the hull components, such as for example, hull panels 17, longitudinal girders floor frames 24 and bulkheads 26 significantly increases the strength of these individual hull components and the hull overall, and allows for a reduction in the thickness of the inner and outer steel plates 34 and 36 in the composite hull panels 18, and a significant reduction in the number of conventional hull construction components, such as stiffening elements 7, frames 11 and support members 2, 3 required to carry the in-plane service loads, such as, for

example, the service loads that cause hogging and sagging. Substitution of the stronger composite panel 18 for conventional steel plates and for conventional frame and support members also simplifies the supporting structure. The stronger composite panels 18 allow construction with significantly fewer structural members, which in turn significantly reduces the number of structural intersections, such as, for example longitudinals passing through floor frames 24, bulkheads 26, frame end brackets (not shown), tripping brackets (not shown), etc. The reduction in structural intersections in turn reduces the number of fatigue sensitive details and the corresponding number of fatigue failures that may occur. Fewer structural members also reduces the chances that a crack will propagate to the inner hull 20 in an accident situation.

The composite plate system combined with innovative naval architecture details provides an impact resistant tough structure. The outer steel plate 36 of the composite panel 18 acts as a hard protective wearing surface. The elastomer core 38 absorbs energy, dissipates transverse loads to the inner steel plate 34 and provides a continuous high elongation thermal resistant membrane. The inner steel plate 34 also serves as a hard protective wearing surface, and carries the majority of the impact load in inelastic membrane action. The sandwich concept allows for the optimum distribution of steel layer thicknesses between the outer and inner steel plates 34 and 36 of the composite panel 18 to provide the most efficient structural system. The thermal insulating properties of the elastomer core 38 provide a warmer environment to the inner steel plate 34 and supporting structural steel elements, such as longitudinal girders 22 and floor frames 24, allowing for the use of less costly lower fracture tough steel. In an accidental or extreme load condition, the ductile elastomer core 38 of the composite panel 18 increases the puncture resistance of the inner and outer metal plates 34 and 36, creates more uniform strain fields within the inner and outer metal plates 34 and 36 as they deform over supporting

elements, such as longitudinal girders 22 and floor frames 24, decreases localized shear deformations, and, in the case of impact loads, greatly enhances the resistance of the inner and outer metal plates 34 and 36 to tearing at transverse support elements. The elastomer core 38 within the inner hull 20 composite panel 18 provides an effective crack arrest layer between the outer hull 28, bottom or side structure that generally sustains damage during a collision or grounding, and the inner steel plates 34 of the inner hull 20 which line the cargo tanks. This crack arrest layer in conjunction with other crack arrest detailing will significantly reduce the likelihood of or even eliminate oil outflow that would occur from cracks propagating into the cargo tank from the rupture of the outer hull.

The simplified structural system is less congested, and with its flat surfaces, it is easier to apply, inspect and maintain protective coatings thereon. Coating breakdown is generally most common in areas which are difficult to access, such as the underside of flanges or flange web intersections (not shown), where the original coating application may be inadequate and subsequent coating maintenance applications are difficult. Because the composite panel system has less surface area to protect, there is a reduced probability of corrosion problems and an increased service life.

The initial cost to build the composite steel-elastomer-steel panel double hull structure is less than its traditional all-steel stiffened plate counterpart. The cost of the elastomer core material, installation and additional welding associated with the composite panels is offset by the elimination of a substantial number of conventional steel plate stiffeners 7, the elimination of support members, such as, for example, collar plates or compensating lugs at longitudinal transverse frame, floor or bulkhead intersections, and the elimination of substantial surface areas which in conventional hulls require painting and maintenance. Further cost benefits are realized in increased service life and lower liability and cargo

insurance costs and lower operating costs that result from a lighter vessel and lower heating costs of oil during transit.

The fundamental reason for double hull oil tankers is to minimize the probability of oil outflow in the case of accidental or extreme load events such as grounding or collisions. In this regard, the inventive system provides superior performance to prior art designs.

Large scale grounding tests on prior art bottom hull sections indicate that rupture of the interior hull of current steel double hull alternatives will occur as a result of crack propagation from the initial rupture of the outside hull, even if the depth of penetration into the hull, by a rock or other object, is less than the separation distance between the inner and outer hulls. It becomes essential to isolate the cargo tank with a crack arresting protection layer 15. Figs. 7-10 illustrate the interconnection of the composite hull plates 18 with the composite transverse bulkhead 26, the composite floor frame 24 and the composite longitudinal girder 22. The composite longitudinal girder 22 extends toward and connects with the composite floor frame 24 beneath the transverse bulkhead 26. The longitudinal edges of the longitudinal girder 22 are connected directly only to the inner plate 34 of the outer hull 28 and the outer plate 36 of the inner hull 20. The spacers 44 are arranged within the composite plate 18 of the inner hull 20 so that they are located midway between longitudinal girders 22. Referring to Fig. 8, a simple fillet weld 48 fastens edge 46 of the spacer 44 to the inner surface 66 of the outer plate 36 of the inner hull 20, and a single butt weld 55 fastens the edges 52 and 54 of inner hull inner plates 35a and 35b, respectively, and edge 50 of spacer 44, joining the respective plates of the composite panel 18. These simplified weld details are configured for ease of fabrication and to facilitate automation of welding operations. The placement of spacers 44 at mid distance between the longitudinal girders 22, in combination with the semi-circular clearance 60 in the floor frame 24 at the

transverse bulkhead 26 adjacent to the location of the spacer 44 in the inner hull panel 20 provides an effective crack arrest barrier. Figs. 8-10 clearly illustrate that the only direct, metal-to-metal contact between the inner metal layer 34 and the outer metal layer 36 of the inner hull 20 is the spacer 44. The inner hull 20 has effectively been isolated from crack propagation effects by placing spacer 44 at a significant distance from longitudinal girders 22, and by providing a clearance 60 in floor frame 24 proximal to the location of spacer 44 in the inner hull composite panel 18. Cracks propagating from the outer hull 28 up through the longitudinal girders 22 are stopped by the elastomer core 38 in the inner hull 20. Cracks propagating from the outer hull 28 up through floor frame 24, or other similar transverse structural members, terminate at clearance 60, effectively preventing the propagation of the crack through spacer 44 to the inner plate 34 of the inner hull 20.

The semi-circular clearance 60 is a typical structural discontinuity that is used to terminate cracks in structures subject to crack propagation due to fatigue. A plug 62 fills the semi-circular clearance 60. The plug 62 has peripheral flanges 64 on either side of the floor frame 24 which create water tight compartments on either side. The plug may, for example, be a cast-in-place elastomer, although other types of plugs are contemplated. Figs. 8, 9 and 10 clearly illustrate that the cargo tank 68 is effectively isolated, by means of the polyurethane elastomer core 38, from the outer ship structure, with the only direct metal-to-metal connection between the inner metal plate 34 of the inner hull 20 and the rest of the ship structure being the spacer elements 44 between inner and outer metal plates 34 and 36 shown in Fig. 8.

As illustrated in Fig. 9, the bulkhead 26 is fastened by welding or other means to the inner plate 34 of inner hull 20. Below the inner hull 20, floor frame 24 supports bulkhead 26 and is fastened by welding or other means to the outer plate 36 of inner hull 20. The elastomer

layer 38 forms a crack arrest layer 15 between the floor frame 24 and the bulkhead 26. In order to ensure that there is no direct metal to metal contact between the inner plate 34 and the outer plate 36 of the inner hull 20, where the inner hull 20 passes between the floor frame 24 and the bulkhead 26, a gap 67 (FIG. 13) may be provided in the longitudinal spacer 44 (shown from a side view in FIG. 13) where it passes between the floor frame 24 and the bulkhead 26 and extending a short distance to either side of the transverse components as marked on page 20. Additional elastomer spacers may be placed transverse to the longitudinal spacers to provide a weld margin about the floor frame 24 and the bulkhead 26. Subsequent to welding gap 67 is filled with elastomer. Gap 67 is subsequently filled with elastomer. This effectively isolates the cargo tank from cracks propagating through the steel that may result from a collision of another vessel into the side structure of the hull.

In addition to innate crack arresting, the present invention also provides increased energy absorption capacity over that of CDH or ADH. The higher concentration of steel plate material in the hull plates coupled with the physical and behavior characteristics of the steel-elastomer-steel sandwich panel, such as increased section modulus and elastic rebounding properties of the elastomer, tend to spread local plasticity, e.g. decreases localized bending and shear strains around sharp or small load points, and with longitudinal girders that are designed to plastically deform (crumple) under accidental or extreme loads, will maximize the material deforming in plastic membrane action, maximize the material in contact with the object struck or striking object, delay the initiation of tearing and increase the energy absorption capacity. The result is a tough skin hull and an oil tanker with greater resistance to impact loads. To ensure survivability, the oil tanker is designed to maintain hull girder integrity after any probable accidental or extreme load event. The simplification of the structural arrangement reduces the

number of intersections of perpendicular framing elements and the number of fatigue prone details.

As a result of providing the simplified structural system illustrated above, there is less surface area to be coated and protected from corrosion, and the surface area that does exist is predominantly flat and unobstructed. The application, inspection and maintenance of protective coatings is therefore easier. All of these factors work to reduce the initial construction costs, in-service maintenance costs and increase the potential service life of the vessel.

The thermal characteristics of the polyurethane elastomer may insulate the inner plate of the outside hull, the plates of the inside hull and the longitudinal girders from ambient temperatures such as, for example, oil tankers operating in cold weather regions, reducing the notch toughness requirements for the steel and the possibility of brittle fracture under impact loads. For the inside hull, this thermal insulation reduces in-service costs associated with heating of the oil cargo in transit.

The elastomer may be selected to be fuel and oil resistant, and impermeable to water. The selected elastomer should fully adhere to the steel plates to which it is cast. If properly selected, the elastomer will prevent the migration of water, fuel or oil between the inner and outer plates of either hull in the event where corrosion or abrasion causes a hole in any part of one of the hull plates.

The inventive system has been designed to be constructable and cost competitive to build and to maintain.

Although a single embodiment which incorporates the teachings of the present invention has been shown and described herein, those skilled in the art can readily devise many other varied embodiment that incorporate these teachings, all of which are within the scope of the present invention.

WHAT IS CLAIMED IS

1. A laminate panel for use in the construction of a containment vessel, said laminate panel comprising:

an outer metal layer;

an inner metal layer; and

an intermediate layer bonded to both said inner and outer metal layers, said intermediate layer comprising a plastic material.

2. The laminate panel of claim 1 further comprising a spacer between said outer metal layer and said inner metal layer.

3. The laminate panel of claim 1 wherein said plastic intermediate layer comprises a polyurethane plastic.

4. The laminate panel of claim 2 wherein said plastic intermediate layer comprises a polyurethane plastic.

5. The laminate panel of claim 3, wherein said outer metal layer comprises steel.

6. The laminate panel of claim 4, wherein said outer metal layer comprises steel.

7. The laminate panel of claim 1, wherein said outer metal layer comprises steel.

8. The laminate panel of claim 2, wherein said outer metal layer comprises steel.

9. The laminate panel of claim 1, wherein said inner metal layer comprises steel.

10. The laminate panel of claim 2, wherein said inner metal layer comprises steel.

11. The laminate panel of claim 7, wherein said inner metal layer comprises steel.

12. The laminate panel of claim 8, wherein said inner metal layer comprises steel.

13. The laminate panel of claim 3, wherein said inner metal layer comprises steel.

14. The laminate panel of claim 4, wherein said inner metal layer comprises steel.

15. A containment vessel comprising:

an outer wall;

an inner wall, located at a first predetermined distance from said outer wall, said inner wall comprising a laminate, said laminate comprising:

an outer metal layer having an inner and outer surface;

an inner metal layer having an inner and outer surface;

a spacer element between said inner surface of said outer metal layer and said outer surface of said inner metal layer, said spacer element arranged to maintain a second predetermined distance between said outer and inner metal layers, said spacer contacting said inner surface of said outer wall; and

an intermediate layer bonded to both said inner and outer metal layers, said intermediate layer comprising a first plastic material; and

a plurality of structural members connecting said outer wall to said outer metal layer of said inner wall, each of said support members having a stress relief clearance adjacent a portion of said outer surface of said inner wall outer metal layer, said clearance being opposite a point where said inner wall outer metal layer inner surface contacts said spacer, said clearance provided to prevent crack propagation directly from said structural

members to said inner metal layer of said inner wall laminate through said spacer.

16. The containment vessel of claim 15 further comprising a deformable plug, said plug substantially filling said clearance in a sealed relationship.

17. The containment vessel of claim 16 wherein said deformable plug comprises a second plastic material.

18. The containment vessel of claim 15 wherein said first plastic material comprises a polyurethane elastomer.

19. The containment vessel of claim 17 wherein said second plastic material comprises a polyurethane elastomer.

20. The containment vessel of claim 15 wherein said inner metal layer comprises steel.

21. The containment vessel of claim 20 wherein said outer metal layer comprises steel.

22. The containment vessel of claim 15 wherein said outer metal layer comprises steel.

23. The containment vessel of claim 18 wherein said inner metal layer comprises steel.

24. The containment vessel of claim 23 wherein said outer metal layer comprises steel.

25. The containment vessel of claim 18 wherein said outer metal layer comprises steel.

26. The containment vessel of claim 19 wherein said inner metal layer comprises steel.

27. The containment vessel of claim 26 wherein said outer metal layer comprises steel.

28. The containment vessel of claim 19 wherein said outer metal layer comprises steel.

29. The containment vessel of claim 15 wherein said spacer element is integrally formed.

30. The containment vessel of claim 15 wherein said spacer element comprises a plurality of spacer members.

31. The containment vessel of claim 15 wherein said outer wall comprises a laminate, said laminate comprising:

an outer metal layer having an inner and outer surface;

an inner metal layer having an inner and outer surface;

a spacer element between said inner surface of said outer metal layer and said outer surface of said inner metal layer, said spacer element arranged to maintain a prescribed distance between said outer and inner metal layers, said spacer contacting said inner surface of said outer wall; and

an intermediate layer bonded to both said inner and outer metal layers, said intermediate layer comprising a plastic material.

32. The containment vessel of claim 31 wherein said plastic material comprises polyurethane elastomer.

33. The containment vessel of claim 31 wherein said inner metal layer comprises steel.

34. The containment vessel of claim 33 wherein said outer metal layer comprises steel.

35. The containment vessel of claim 31 wherein said outer metal layer comprises steel.

36. The containment vessel of claim 32 wherein said inner metal layer comprises steel.

37. The containment vessel of claim 36 wherein said outer metal layer comprises steel.

38. The containment vessel of claim 32 wherein said outer metal layer comprises steel.

39. A laminate for use in the construction of a containment vessel of the type including an inner wall, an outer wall, and a plurality of structural members between said inner and outer wall, said inner and outer walls being spaced a first predetermined distance from each other by said structural members, said laminate comprising:

an outer metal layer;

an inner metal layer;

a spacer element between said inner and outer metal layer, said spacer element arranged to maintain a second predetermined distance between said outer and inner metal layers;

an intermediate layer bonded to both said inner and outer metal layers, said intermediate layer comprising a plastic material; and

wherein each structural member has a stress relief clearance opposite said spacer element.

40. The laminate panel of claim 5, wherein said inner metal layer comprises steel.

41. The laminate panel of claim 6, wherein said inner metal layer comprises steel.

FIG. 1
PRIOR ART

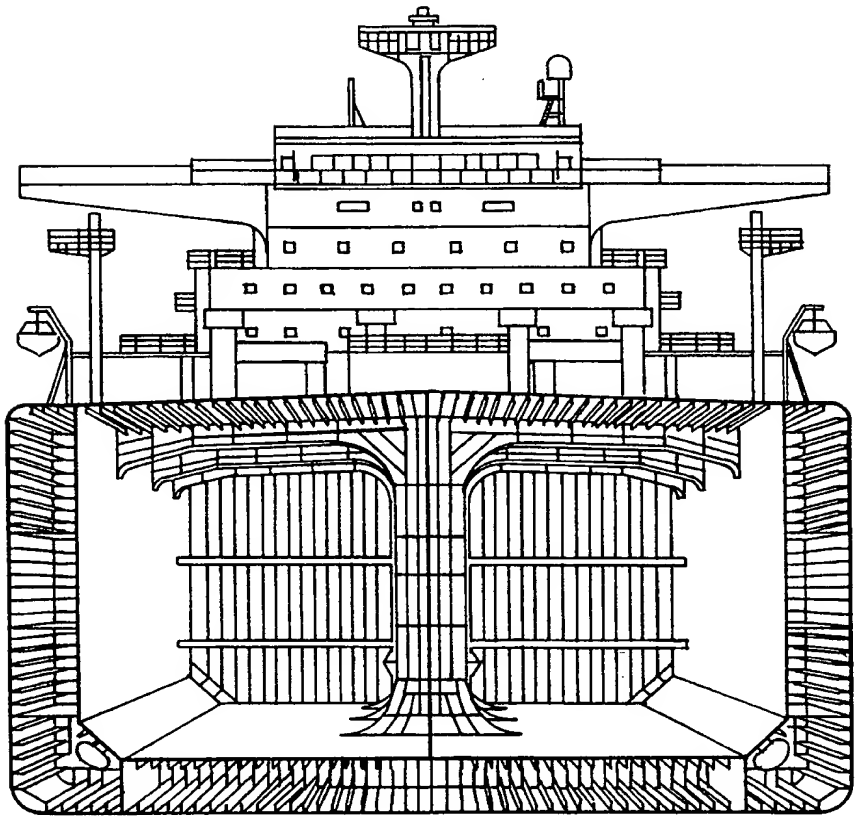


FIG. 2
PRIOR ART

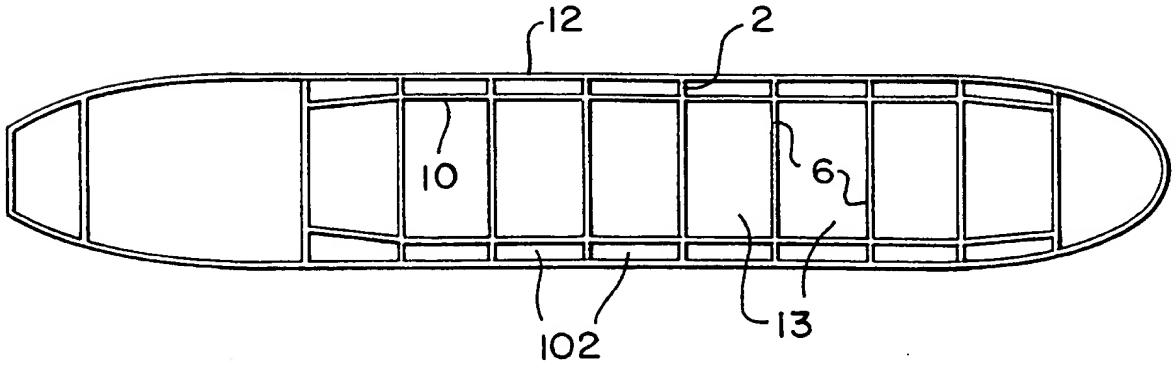


FIG. 3
PRIOR ART

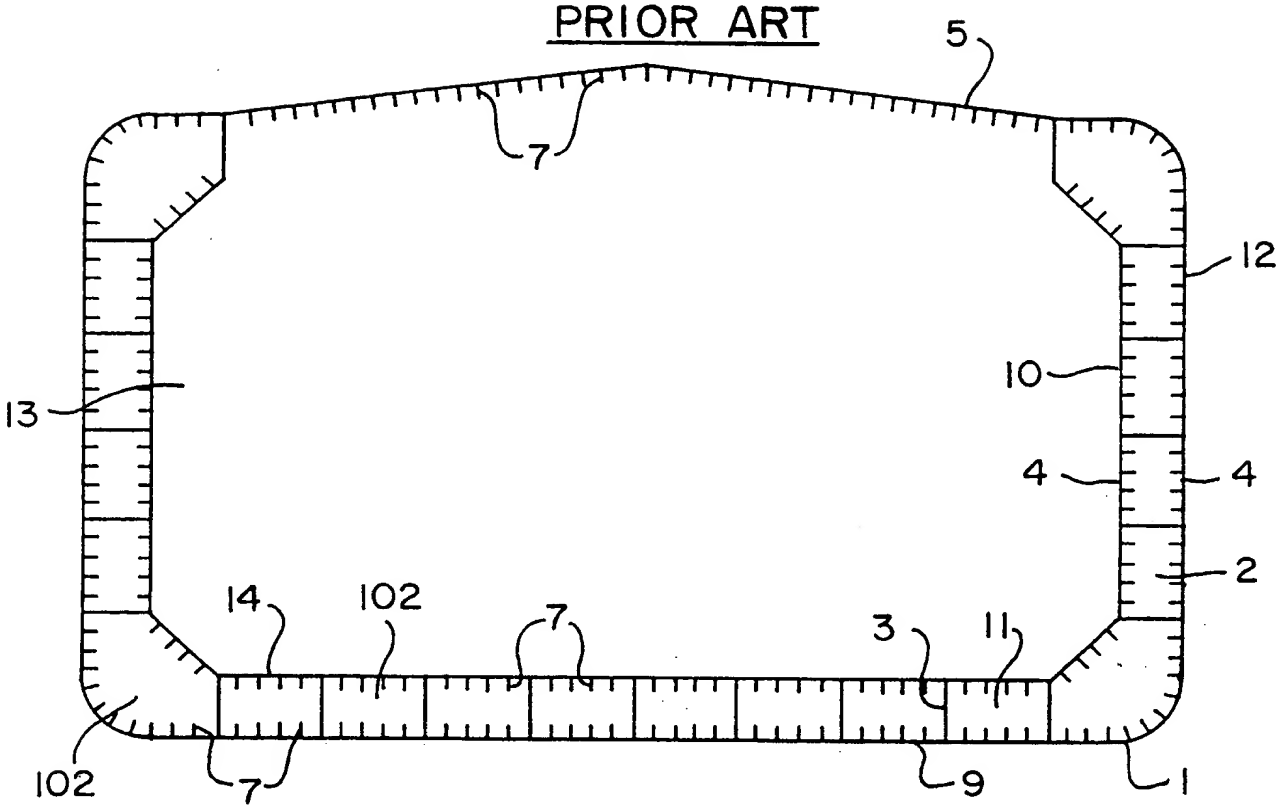


FIG. 4

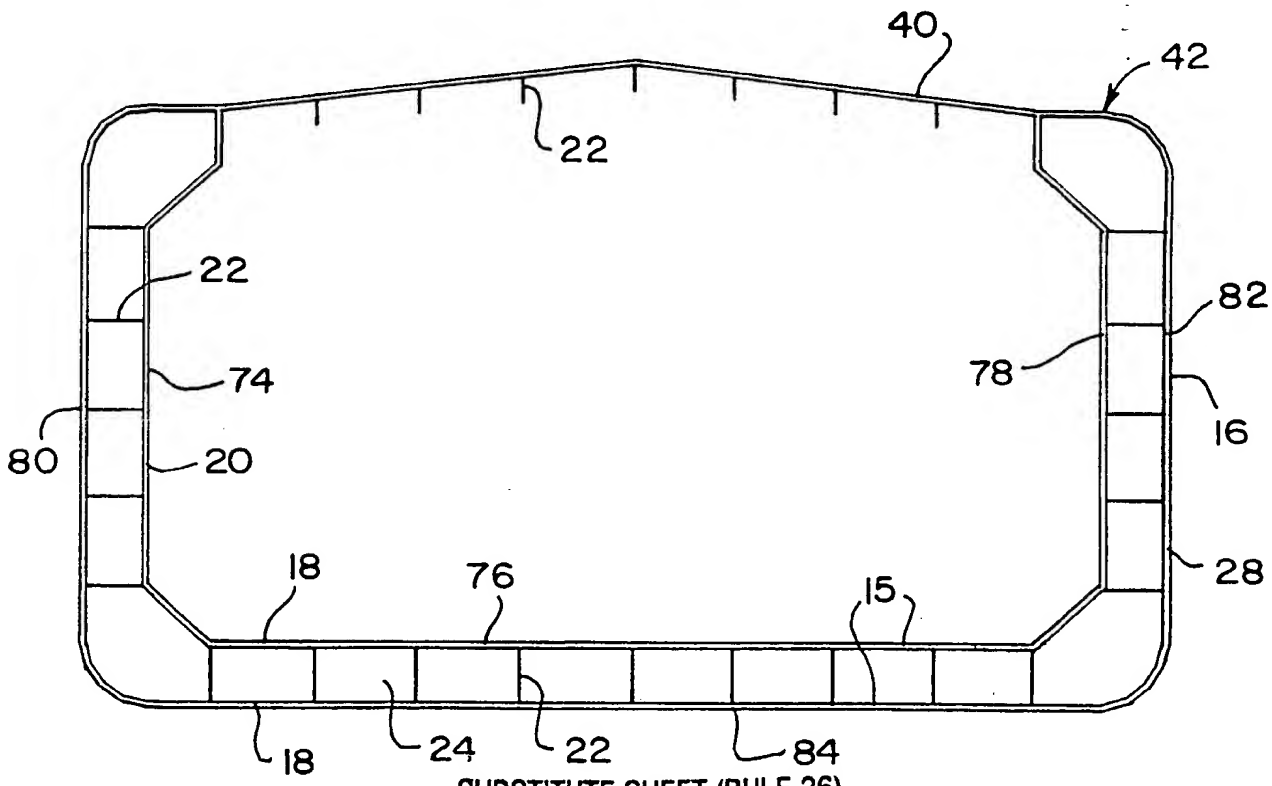


FIG. 5

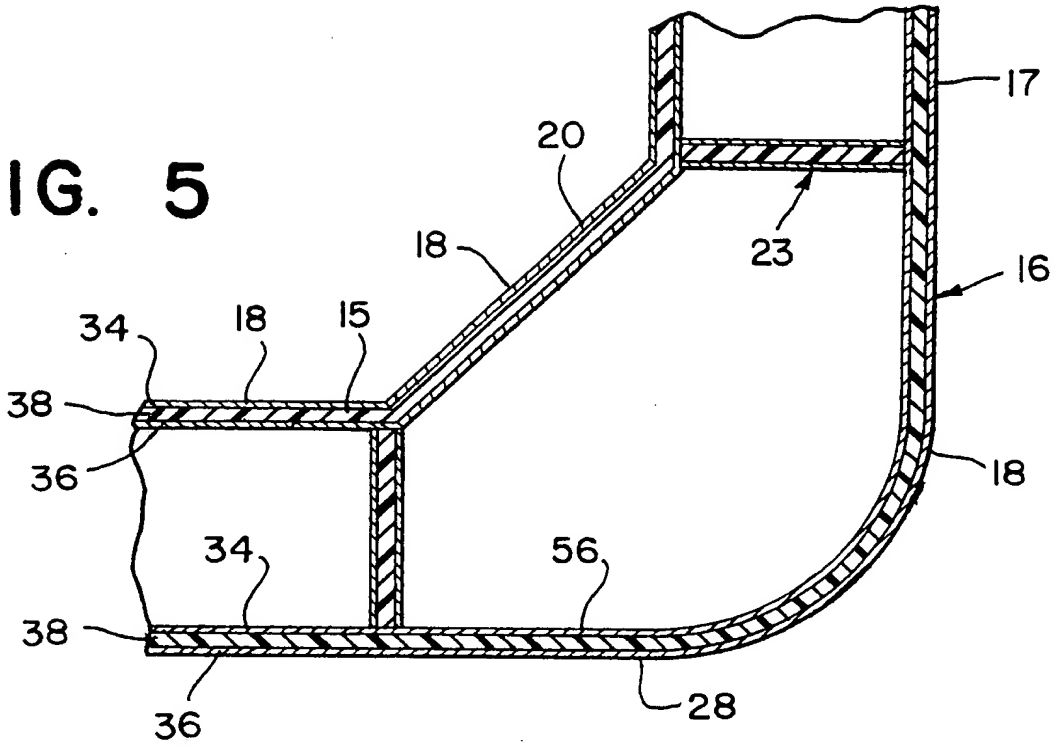


FIG. 6

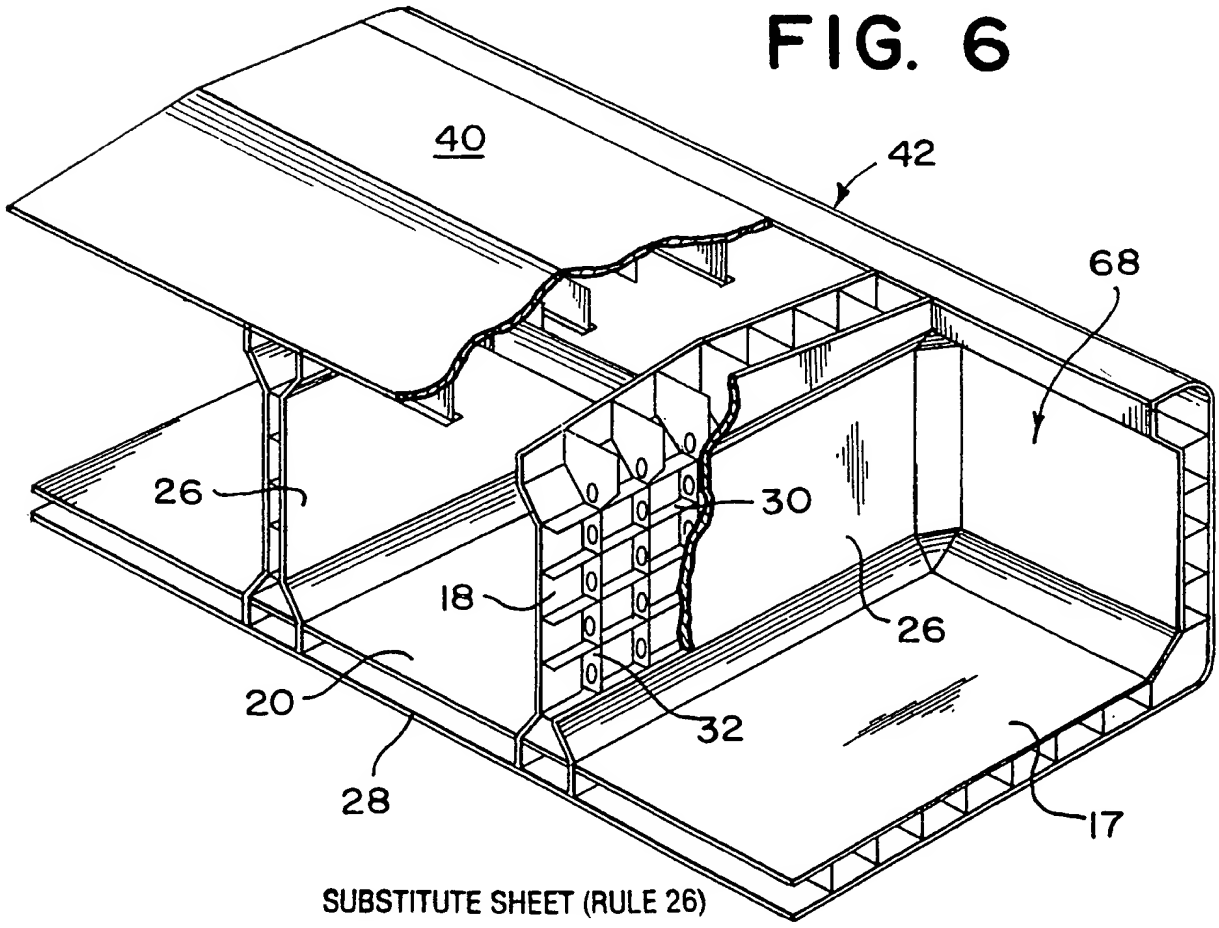


FIG. 7

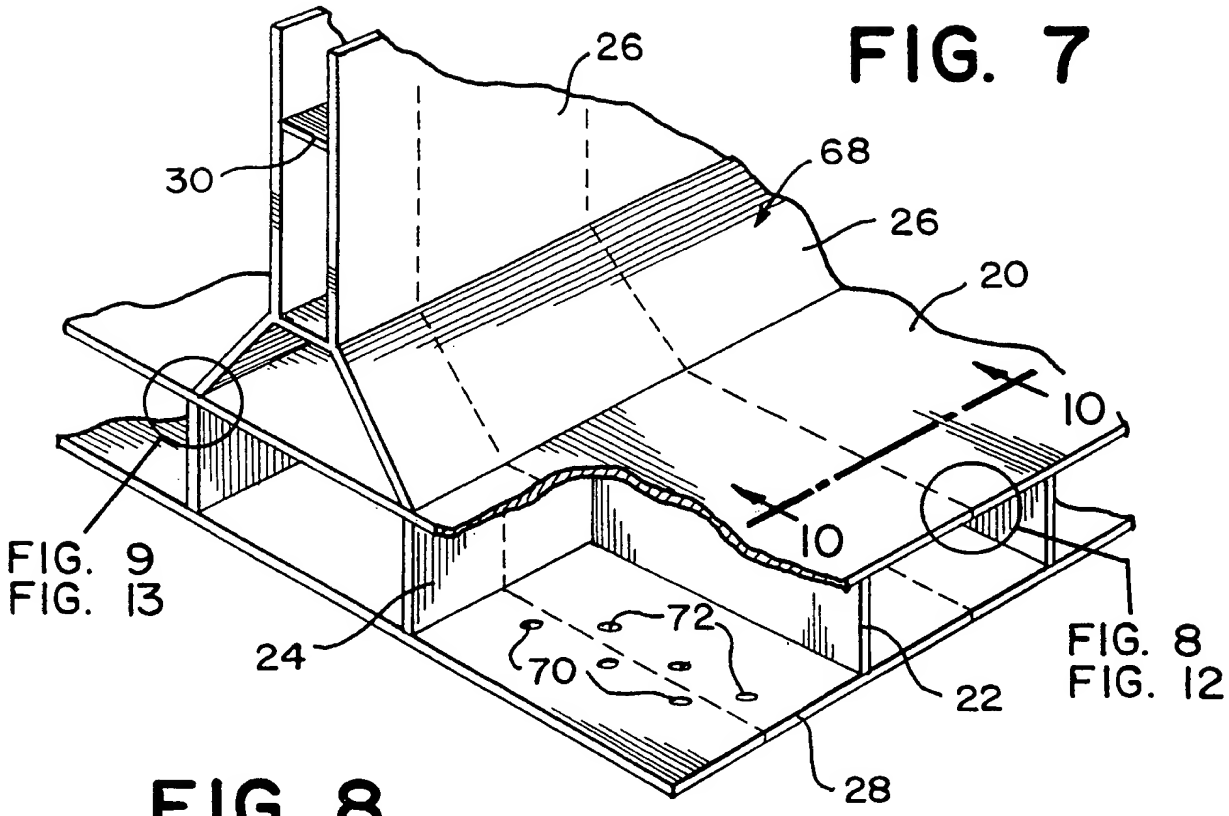


FIG. 8

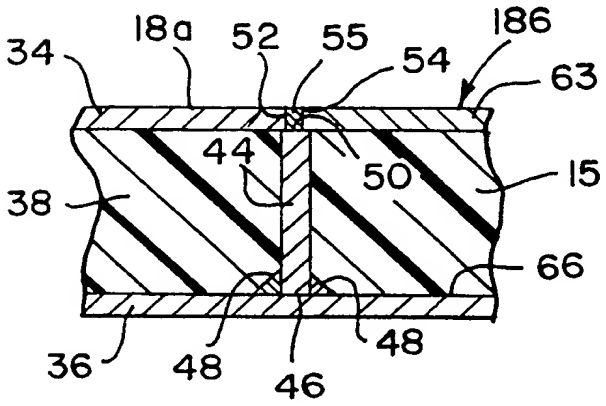


FIG. 9

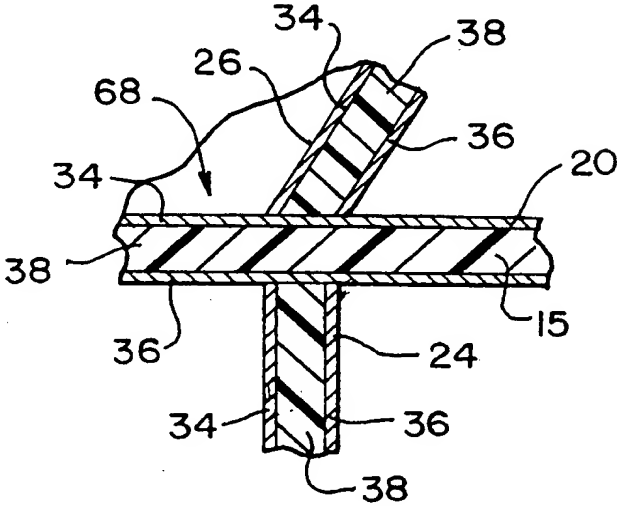
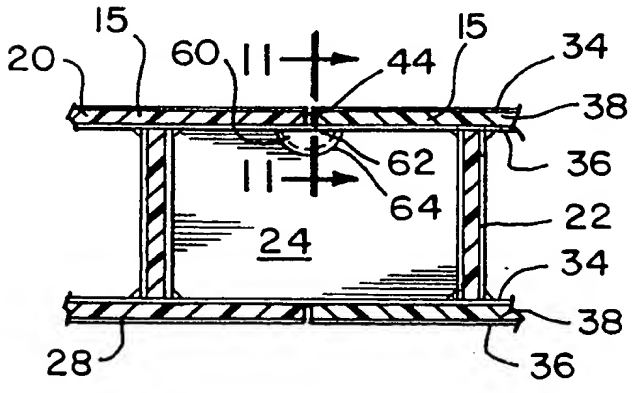


FIG. 10



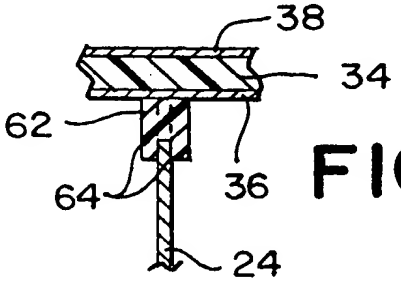


FIG. 11

FIG. 12

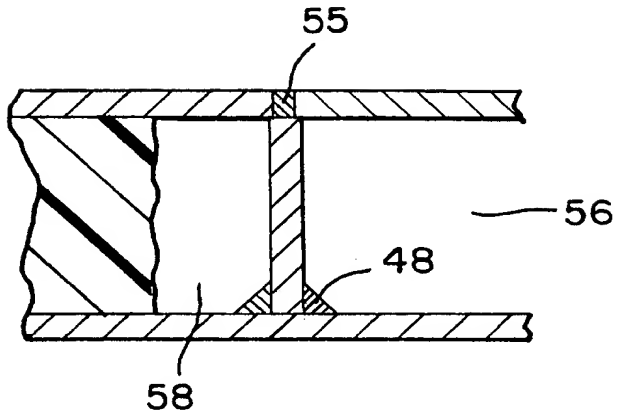
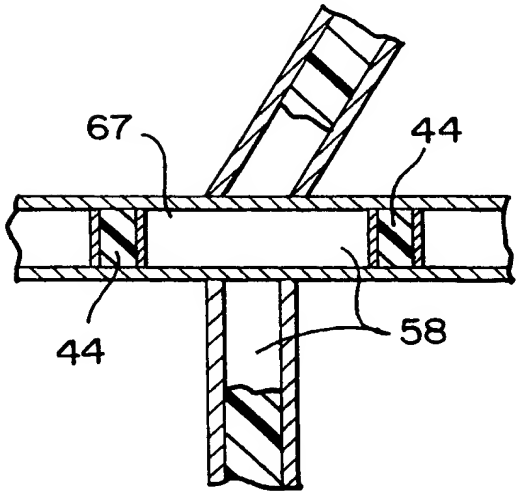


FIG. 13



INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 97/01426

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B15/08 B63B5/24 B63B3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B32B B63B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 30 05 015 A (OLBRICH KURT) 20 August 1981 see claims; figure 1	1-14
A	---	15,39
X	US 3 732 138 A (ALMOG E) 8 May 1973 see the whole document	1-14
A	---	15
X	US 4 116 150 A (MCCOWN THOMAS E) 26 September 1978 see column 4, line 24 - column 5, line 11; figures 1-3	1-14
A	---	15
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
9 March 1998	25/03/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ibarrola Torres, O

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 97/01426

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 911 190 A (MYERS ROBERT A ET AL) 7 October 1975 see column 1, line 10 - line 21 see column 10, line 7 - line 21; claims 1,2	1,3,5,7, 9,11,13
X	US 4 739 722 A (ROGSTAD KEITH L) 26 April 1988 see column 3, line 24 - column 4, line 13; figures	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IB 97/01426

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3005015 A	20-08-81	NONE	
US 3732138 A	08-05-73	NONE	
US 4116150 A	26-09-78	BE 852234 A	08-09-77
		DE 2710338 A	15-09-77
		FI 770762 A	10-09-77
		FR 2343965 A	07-10-77
		GB 1541806 A	07-03-79
		JP 52121811 A	13-10-77
		NL 7702568 A	13-09-77
		NL 8200020 A,B,	03-05-82
		SE 434183 B	09-07-84
		SE 7702227 A	10-09-77
		US 4170952 A	16-10-79
US 3911190 A	07-10-75	AU 8776475 A	30-06-77
		BE 836937 A	22-06-76
		CA 1054917 A	22-05-79
		DE 2557824 A	24-06-76
		FR 2295839 A	23-07-76
		GB 1505299 A	30-03-78
		JP 973943 C	19-10-79
		JP 51089584 A	05-08-76
		JP 54006076 B	24-03-79
US 4739722 A	26-04-88	US 4850297 A	25-07-89

CORRECTED VERSION*

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
B32B 15/08, B63B 5/24, 3/20

A1

(11) International Publication Number: WO 98/21029

(43) International Publication Date: 22 May 1998 (22.05.98)

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(22) International Filing Date: 12 November 1997 (12.11.97)

(30) Priority Data:
08/746,539 13 November 1996 (13.11.96) US

(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application
US 08/746,539 (CON)
Filed on 13 November 1996 (13.11.96)

(71) Applicant *(for all designated States except US)*: FERN INVESTMENTS LIMITED [-/-]; Ordnance House, 31 Pier Road, St. Helier, Jersey, Channel Islands (GB).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: KENNEDY, Stephen, J. [CA/CA]; 42 Hampton Avenue, Ottawa, Ontario K1Y 0N2 (CA).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: COMPOSITE STEEL STRUCTURAL PLASTIC SANDWICH PLATE SYSTEMS

(57) Abstract

A composite laminate panel suitable for building containment vessels, and in particular, suitable for building double hull oil tankers. The laminate has two facing metal layers structurally bonded to a polyurethane elastomer core. The laminate is used in various hull components, such as the hull plates, longitudinal girders, transverse frames and bulkheads. The laminate is used to build the inner hull and outer hull, and may be used to build the structural supports between the inner and outer hulls. The innermost layer of inner hull contains the ship's cargo. The elastomer core of the inner hull laminate isolates the innermost hull skin from cracks, thereby preventing a loss of cargo such as oil into the environment, when the outer hull is pierced, penetrated or ruptured in an accident or grounding.

*(Referred to in PCT Gazette No. 38/1998, Section II)

BNSDOCID: <WO 9821029A1>

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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EE	Estonia	LR	Liberia	SG	Singapore		

09701963 EO/US
PCT/EP99/03545

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing: 16 December 1999 (16.12.99)	
International application No.: PCT/EP99/03545	Applicant's or agent's file reference: 0050/049096
International filing date: 22 May 1999 (22.05.99)	Priority date: 05 June 1998 (05.06.98)
Applicant: WILD, Heike et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International preliminary Examining Authority on:

02 October 1999 (02.10.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: J. Zahra
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

Form PCT/IB 331 (July 1992)

3001825

VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

PCT

INTERNATIONALER RECHERCHENBERICHT

(Artikel 18 sowie Regeln 43 und 44 PCT)

Aktenzeichen des Anmelders oder Anwalts	**WEITERES VORGEHEN**	siehe Mitteilung über die Übermittlung des internationalen Recherchenberichts (Formblatt PCT/ISA/220) sowie, soweit zutreffend, nachstehender Punkt 5
0050/049096		
Internationales Aktenzeichen	Internationales Anmeldedatum *(Tag/Monat/Jahr)*	(Frühestes) Prioritätsdatum *(Tag/Monat/Jahr)*
PCT/EP 99/03545	22/05/1999	05/06/1998
Anmelder		
BASF AKTIENGESELLSCHAFT		

Dieser internationale Recherchenbericht wurde von der Internationalen Recherchenbehörde erstellt und wird dem Anmelder gemäß Artikel 18 übermittelt. Eine Kopie wird dem Internationalen Büro übermittelt.

Dieser internationale Recherchenbericht umfaßt insgesamt 3 Blätter.

[X] Darüber hinaus liegt ihm jeweils eine Kopie der in diesem Bericht genannten Unterlagen zum Stand der Technik bei.

1. **Grundlage des Berichts**

   a. Hinsichtlich der **Sprache** ist die internationale Recherche auf der Grundlage der internationalen Anmeldung in der Sprache durchgeführt worden, in der sie eingereicht wurde, sofern unter diesem Punkt nichts anderes angegeben ist.

   [ ] Die internationale Recherche ist auf der Grundlage einer bei der Behörde eingereichten Übersetzung der internationalen Anmeldung (Regel 23.1 b)) durchgeführt worden.

   b. Hinsichtlich der in der internationalen Anmeldung offenbarten **Nucleotid- und/oder Aminosäuresequenz** ist die internationale Recherche auf der Grundlage des Sequenzprotokolls durchgeführt worden, das

   [ ] in der internationalen Anmeldung in Schriftlicher Form enthalten ist.

   [ ] zusammen mit der internationalen Anmeldung in computerlesbarer Form eingereicht worden ist.

   [ ] bei der Behörde nachträglich in schriftlicher Form eingereicht worden ist.

   [ ] bei der Behörde nachträglich in computerlesbarer Form eingereicht worden ist.

   [ ] Die Erklärung, daß das nachträglich eingereichte schriftliche Sequenzprotokoll nicht über den Offenbarungsgehalt der internationalen Anmeldung im Anmeldezeitpunkt hinausgeht, wurde vorgelegt.

   [ ] Die Erklärung, daß die in computerlesbarer Form erfaßten Informationen dem schriftlichen Sequenzprotokoll entsprechen, wurde vorgelegt.

2. [ ] **Bestimmte Ansprüche haben sich als nicht recherchierbar erwiesen** (siehe Feld I).

3. [ ] **Mangelnde Einheitlichkeit der Erfindung** (siehe Feld II).

4. Hinsichtlich der **Bezeichnung der Erfindung**

   [X] wird der vom Anmelder eingereichte Wortlaut genehmigt.

   [ ] wurde der Wortlaut von der Behörde wie folgt festgesetzt:

5. Hinsichtlich der **Zusammenfassung**

   [X] wird der vom Anmelder eingereichte Wortlaut genehmigt.

   [ ] wurde der Wortlaut nach Regel 38.2b) in der in Feld III angegebenen Fassung von der Behörde festgesetzt. Der Anmelder kann der Behörde innerhalb eines Monats nach dem Datum der Absendung dieses internationalen Recherchenberichts eine Stellungnahme vorlegen.

6. Folgende Abbildung der **Zeichnungen** ist mit der Zusammenfassung zu veröffentlichen: Abb. Nr. ---

   [ ] wie vom Anmelder vorgeschlagen

   [ ] weil der Anmelder selbst keine Abbildung vorgeschlagen hat.

   [ ] weil diese Abbildung die Erfindung besser kennzeichnet.

   [ ] keine der Abb.

INTERNATIONALER RECHERCHENBERICHT

Internationales Aktenzeichen
PCT/EP 99/03545

A. KLASSIFIZIERUNG DES ANMELDUNGSGEGENSTANDES
IPK 6 B32B17/08 C08G18/48 B63B3/00

Nach der Internationalen Patentklassifikation (IPK) oder nach der nationalen Klassifikation und der IPK

B. RECHERCHIERTE GEBIETE

Recherchierter Mindestprüfstoff (Klassifikationssystem und Klassifikationssymbole)
IPK 6 C08G B32B B63B

Recherchierte aber nicht zum Mindestprüfstoff gehörende Veröffentlichungen, soweit diese unter die recherchierten Gebiete fallen

Während der internationalen Recherche konsultierte elektronische Datenbank (Name der Datenbank und evtl. verwendete Suchbegriffe)

C. ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie°	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	WO 98 21029 A (KENNEDY STEPHEN J ;FERN INVESTMENTS LIMITED (CA)) 22. Mai 1998 (1998-05-22) Seite 12, Zeile 20 - Seite 19, Zeile 14 Ansprüche 1,3 ---	1,5-10
A	EP 0 405 300 A (CHISSO CORP) 2. Januar 1991 (1991-01-02) Seite 2, Zeile 42 - Seite 3, Zeile 25 Beispiel 1 ---	1
A	US 4 859 523 A (ENDOH HIROSHI ET AL) 22. August 1989 (1989-08-22) Spalte 7, Zeile 41 - Spalte 8, Zeile 64 Ansprüche 1,9 ---	1

-/--

[X] Weitere Veröffentlichungen sind der Fortsetzung von Feld C zu entnehmen

[X] Siehe Anhang Patentfamilie

° Besondere Kategorien von angegebenen Veröffentlichungen :
"A" Veröffentlichung, die den allgemeinen Stand der Technik definiert, aber nicht als besonders bedeutsam anzusehen ist
"E" älteres Dokument, das jedoch erst am oder nach dem internationalen Anmeldedatum veröffentlicht worden ist
"L" Veröffentlichung, die geeignet ist, einen Prioritätsanspruch zweifelhaft erscheinen zu lassen, oder durch die das Veröffentlichungsdatum einer anderen im Recherchenbericht genannten Veröffentlichung belegt werden soll oder die aus einem anderen besonderen Grund angegeben ist (wie ausgeführt)
"O" Veröffentlichung, die sich auf eine mündliche Offenbarung, eine Benutzung, eine Ausstellung oder andere Maßnahmen bezieht
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"X" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann allein aufgrund dieser Veröffentlichung nicht als neu oder auf erfinderischer Tätigkeit beruhend betrachtet werden
"Y" Veröffentlichung von besonderer Bedeutung; die beanspruchte Erfindung kann nicht als auf erfinderischer Tätigkeit beruhend betrachtet werden, wenn die Veröffentlichung mit einer oder mehreren anderen Veröffentlichungen dieser Kategorie in Verbindung gebracht wird und diese Verbindung für einen Fachmann naheliegend ist
"&" Veröffentlichung, die Mitglied derselben Patentfamilie ist

Datum des Abschlusses der internationalen Recherche	Absendedatum des internationalen Recherchenberichts
1. September 1999	16/09/1999

Name und Postanschrift der Internationalen Recherchenbehörde	Bevollmächtigter Bediensteter
Europäisches Patentamt, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Neugebauer, U

1

Formblatt PCT/ISA/210 (Blatt 2) (Juli 1992)

Internationales Aktenzeichen
PCT/EP 99/03545

C.(Fortsetzung) ALS WESENTLICH ANGESEHENE UNTERLAGEN

Kategorie°	Bezeichnung der Veröffentlichung, soweit erforderlich unter Angabe der in Betracht kommenden Teile	Betr. Anspruch Nr.
A	DATABASE WPI Section Ch, Week 9443 Derwent Publications Ltd., London, GB; Class A25, AN 94-347175 XP002113984 & JP 06 271639 A (INOAC CORP KK), 27. September 1994 (1994-09-27) Zusammenfassung ---	1,2,4,6, 7,9
A	US 4 547 561 A (WEGNER CHRISTIAN) 15. Oktober 1985 (1985-10-15) Spalte 1, Zeile 62 - Spalte 3, Zeile 55 Beispiel 3 -----	1,2

1

INTERNATIONAL SEARCH REPORT

[redacted]ation on patent family members

[redacted]rnational Application No
[redacted]T/EP 99/03545

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9821029 A	22-05-1998	US 5778813 A	14-07-1998
		AU 4720497 A	03-06-1998
		EP 0938410 A	01-09-1999
		NO 992318 A	13-07-1999
EP 0405300 A	02-01-1991	DE 69013767 D	08-12-1994
		DE 69013767 T	13-04-1995
		JP 3121115 A	23-05-1991
US 4859523 A	22-08-1989	JP 1979057 C	17-10-1995
		JP 4055604 B	03-09-1992
		JP 63048321 A	01-03-1988
JP 6271639 A	27-09-1994	NONE	
US 4547561 A	15-10-1985	DE 3329392 A	28-02-1985
		EP 0133537 A	27-02-1985
		JP 60055020 A	29-03-1985

M.H

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VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS

PCT

INTERNATIONALER VORLÄUFIGER PRÜFUNGSBERICHT

(Artikel 36 und Regel 70 PCT)

Aktenzeichen des Anmelders oder Anwalts	**WEITERES VORGEHEN**	siehe Mitteilung über die Übersendung des internationalen vorläufigen Prüfungsbericht (Formblatt PCT/IPEA/416)
0050/049096		
Internationales Aktenzeichen	Internationales Anmeldedatum *(Tag/Monat/Jahr)*	Prioritätsdatum *(Tag/Monat/Tag)*
PCT/EP99/03545	22/05/1999	05/06/1998
Internationale Patentklassifikation (IPK) oder nationale Klassifikation und IPK		
B32B17/08		
Anmelder		
BASF AKTIENGESELLSCHAFT		

1. Dieser internationale vorläufige Prüfungsbericht wurde von der mit der internationale vorläufigen Prüfung beauftragte Behörde erstellt und wird dem Anmelder gemäß Artikel 36 übermittelt.

2. Dieser BERICHT umfaßt insgesamt 3 Blätter einschließlich dieses Deckblatts.

   ☐ Außerdem liegen dem Bericht ANLAGEN bei; dabei handelt es sich um Blätter mit Beschreibungen, Ansprüchen und/oder Zeichnungen, die geändert wurden und diesem Bericht zugrunde liegen, und/oder Blätter mit vor dieser Behörde vorgenommenen Berichtigungen (siehe Regel 70.16 und Abschnitt 607 der Verwaltungsrichtlinien zum PCT).

   Diese Anlagen umfassen insgesamt Blätter.

3. Dieser Bericht enthält Angaben zu folgenden Punkten:

   - I ☒ Grundlage des Berichts
   - II ☐ Priorität
   - III ☐ Keine Erstellung eines Gutachtens über Neuheit, erfinderische Tätigkeit und gewerbliche Anwendbarkeit
   - IV ☐ Mangelnde Einheitlichkeit der Erfindung
   - V ☒ Begründete Feststellung nach Artikel 35(2) hinsichtlich der Neuheit, der erfinderische Tätigkeit und der gewerbliche Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung
   - VI ☐ Bestimmte angeführte Unterlagen
   - VII ☐ Bestimmte Mängel der internationalen Anmeldung
   - VIII ☐ Bestimmte Bemerkungen zur internationalen Anmeldung

Datum der Einreichung des Antrags	Datum der Fertigstellung dieses Berichts
02/10/1999	21.01.2000
Name und Postanschrift der mit der internationalen vorläufigen Prüfung beauftragten Behörde:	Bevollmächtigter Bediensteter
Europäisches Patentamt D-80298 München Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Schambeck, W Tel. Nr. +49 89 2399 2135

Formblatt PCT/IPEA/409 (Deckblatt) (Januar 1994)

INTERNATIONALER VORLÄUFIGER PRÜFUNGSBERICHT

Internationales Aktenzeichen PCT/EP99/03545

I. Grundlage des Berichts

1. Dieser Bericht wurde erstellt auf der Grundlage (*Ersatzblätter, die dem Anmeldeamt auf eine Aufforderung nach Artikel 14 hin vorgelegt wurden, gelten im Rahmen dieses Berichts als "ursprünglich eingereicht" und sind ihm nicht beigefügt, weil sie keine Änderungen enthalten.*):

Beschreibung, Seiten:

1-14 ursprüngliche Fassung

Patentansprüche, Nr.:

1-10 ursprüngliche Fassung

2. Aufgrund der Änderungen sind folgende Unterlagen fortgefallen:

☐ Beschreibung, Seiten:
☐ Ansprüche, Nr.:
☐ Zeichnungen, Blatt:

3. ☐ Dieser Bericht ist ohne Berücksichtigung (von einigen) der Änderungen erstellt worden, da diese aus den angegebenen Gründen nach Auffassung der Behörde über den Offenbarungsgehalt in der ursprünglich eingereichten Fassung hinausgehen (Regel 70.2(c)):

4. Etwaige zusätzliche Bemerkungen:

V. Begründete Feststellung nach Artikel 35(2) hinsichtlich der Neuheit, der erfinderischen Tätigkeit und der gewerblichen Anwendbarkeit; Unterlagen und Erklärungen zur Stützung dieser Feststellung

1. Feststellung

Neuheit (N)	Ja:	Ansprüche	1-10
	Nein:	Ansprüche	
Erfinderische Tätigkeit (ET)	Ja:	Ansprüche	1-10
	Nein:	Ansprüche	
Gewerbliche Anwendbarkeit (GA)	Ja:	Ansprüche	1-10
	Nein:	Ansprüche	

2. Unterlagen und Erklärungen

si he B iblatt

Die erfindungsgemäßen Verbundelemente, die nach den Angaben in der Beschreibung der Anmeldung insbesondere zur Verwendung im Schiffbau bestimmt sind, weisen eine zwischen 2 Metallschichten angeordnete Schicht aus einem Polyisocyanat-Polyadditionsprodukt der im unabhängigen Anspruch 1 definierten Art auf.

Den im Recherchenbericht genannten Dokumenten sind keinerlei Hinweise zu entnehmen, die den Fachmann hätten veranlassen können, Polyetherpolyalkohole zur Herstellung der Polyisocyanat-Polyadditionsprodukte einzusetzen, um dadurch die auf Seite 2 der Beschreibung, Zeilen 19 bis 33 herausgestellten Vorteile zu erzielen.

09/701963
0130

Translation

5

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 0050/049096	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/EP99/03545	International filing date (*day/month/year*) 22 May 1999 (22.05.99)	Priority date (*day/month/year*) 05 June 1998 (05.06.98)
International Patent Classification (IPC) or national classification and IPC B32B 17/08		
Applicant BASF AKTIENGESELLSCHAFT		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
02 October 1999 (02.10.99)	21 January 2000 (21.01.2000)
Name and mailing address of the IPEA/EP Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/EP99/03545

I. Basis of the report

1. This report has been drawn on the basis of (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

☐ the international application as originally filed.

☒ the description, pages 1-14, as originally filed,
pages _____, filed with the demand,
pages _____, filed with the letter of _____,
pages _____, filed with the letter of _____.

☒ the claims, Nos. 1-10, as originally filed,
Nos. _____, as amended under Article 19,
Nos. _____, filed with the demand,
Nos. _____, filed with the letter of _____,
Nos. _____, filed with the letter of _____.

☐ the drawings, sheets/fig _____, as originally filed,
sheets/fig _____, filed with the demand,
sheets/fig _____, filed with the letter of _____,
sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/fig _____

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-10	YES
	Claims		NO
Inventive step (IS)	Claims	1-10	YES
	Claims		NO
Industrial applicability (IA)	Claims	1-10	YES
	Claims		NO

2. Citations and explanations

The composite elements provided for by the invention, which according to the description of the application are intended in particular for use in shipbuilding, have a layer made of a polyisocyanate polyaddition product of the type defined in independent Claim 1, said layer being disposed between two metal layers.

The documents cited in the search report do not suggest anything which might have prompted a person skilled in the art to use polyether polyols for the preparation of the polyisocyanate polyaddition products so as to obtain the advantages indicated on page 2, lines 19-33, of the description.

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Translation

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference MJPcb644/39	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/FR99/01342	International filing date (*day/month/year*) 08 June 1999 (08.06.99)	Priority date (*day/month/year*) 08 June 1998 (08.06.98)
International Patent Classification (IPC) or national classification and IPC C07K 14/415		
Applicant CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE (CNRS)		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 7 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☒ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
28 December 1999 (28.12.99)	07 September 2000 (07.09.2000)
Name and mailing address of the IPEA/EP Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/FR99/01342

I. Basis of the report

1. This report has been drawn on the basis of (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

☐ the international application as originally filed.

☒ the description, pages 1-23, as originally filed,
pages _____, filed with the demand,
pages _____, filed with the letter of _____,
pages _____, filed with the letter of _____.

☒ the claims, Nos. 1-11, as originally filed,
Nos. _____, as amended under Article 19,
Nos. _____, filed with the demand,
Nos. _____, filed with the letter of _____,
Nos. _____, filed with the letter of _____.

☒ the drawings, sheets/fig 1/8-8/8, as originally filed,
sheets/fig _____, filed with the demand,
sheets/fig _____, filed with the letter of _____,
sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/fig _____

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: II

3.

The documents DATABASE EMBL NUCLEOTIDE AND PROTEIN SEQUENCES, 28 September 1998, accession number: AJ224078 and DATABASE EMBL NUCLEOTIDE AND PROTEIN SEQUENCES, 6 April 1999, accession number: AF079404 have been cited as P documents.
The International Preliminary Examining Authority considers, however, that the priority claimed by the present application is valid. Consequently, these documents have not been taken into account in drawing up the present report.

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	6-11	**YES**
	Claims	1-5	**NO**
Inventive step (IS)	Claims	8-11	**YES**
	Claims	1-7	**NO**
Industrial applicability (IA)	Claims	1-11	**YES**
	Claims	NONE	**NO**

2. Citations and explanations

Reference is made to the following documents:

D1: PLANT MOLECULAR BIOLOGY, Vol.34, No.2, 1 May 1997, pages 325-330, Luo et al. 'Cloning and characterisation of a carrot cDNA coding for a WD repeat protein homologous to Drosophila fizzy, human p55CDC and yeast CDC20 proteins', cited in the application;

D2: WO-A-95/21917.

1. In view of the opinion stated in **Box VIII-1**, the protein described in **D1** is considered to be a plant protein with WD40 repeat motifs related to the FZR sub-family.
It should be noted that, in line with this reasoning, the other proteins indicated in Figure 1B of the present application but also the human p55CDC and CDC20 proteins of *S. cerevisiae* disclosed in **D2** fall within the scope of **Claim 1**.
Consequently, the subject matter of **Claim 1** does not satisfy the criterion of novelty of PCT Article 33(2).

2. **Claim 2** refers to a protein as defined in Claim 1, with at least 45% identity or at least 60%

similarity to SEQ ID No:2. **Dependent** Claim **2** does not contain any feature which, in combination with those of Claim 1, defines a subject satisfying the requirements of the PCT as regards novelty, for the following reason:
The protein sequence described in **D1** is (according to the applicant itself, see page 4, lines 23 to 31) 63% similar (i.e. "at least 60%") to SEQ ID No:2.

3. **Claim 3** refers to a nucleic acid fragment coding for the protein of Claims 1 or 2, or its complementary sequence. **D1** describes such a fragment (see title). Consequently, the subject matter of **Claim 3** does not satisfy the criterion of novelty of PCT Article 33(2).

4. Similarly, **D1** describes vectors containing said nucleic acids but also implicitly *E.coli* bacteria transformed with these vectors (see the annotation to Figure 1 and the techniques used). Consequently, the subject matter of **Claims 4 and 5** does not satisfy the criterion of novelty of PCT Article 33(2).

5. **Claim 6** specifies that the transformed cell is a plant cell. **Claim 7** refers to a transgenic plant transformed by the nucleic acid of Claim 3. None of the available documents describes such cells or plants. Consequently, the subject matter of Claims 6 and 7 satisfies the criterion of novelty of PCT Article 33(2).
However, the production of plant cells and plants transformed by a vector comprising a known gene is common laboratory practice which does not involve an inventive step (PCT Article 33(3)).

6. **Claim 8** refers to the use of a protein according to Claims 1 or 2 for regulating the differentiation and proliferation of plant cells. None of the available documents either describes such a use or allows it to be derived therefrom.
Consequently, the subject matter of **Claims 8 to 10** and of **Claim 11** (see nevertheless Box **VIII-3**) satisfies the criteria of novelty of PCT Article 33(2) and of inventive step of PCT Article 33(3).

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

1. **Claim 1** attempts to define a protein in terms of its:
(i) origin ("plant"),
(ii) vague features ("with WD40 repeat motifs"),
(iii) belonging to a family of proteins (FZR).
Although certain proteins have been classified *a posteriori* in a generic group called "proteins with WD40 repeat motifs" based on certain homologies of sequences which probably define similar structures, the low rate of homology of these fields between different proteins and the variety of the sequences concerned make the definition of a protein simply in terms of the fact that it contains "WD40 repeat motifs" impossible *a priori*.
While the term "FZR sub-family" clearly refers to a protein series known to a person skilled in the art, it does not enable the protein envisaged to be defined clearly. Furthermore, the criteria used for the definition, as proposed in the present application (see Figure 1A and page 5, lines 10 to 15), of the FZR family appear to be rather loose (in view of Figure 1A, it is difficult to understand how the proteins ScHCT1 and SpSRW1 can form part, together with CCS52Ms, of a "sub-family representing a branch which has evolved separately from that consisting of the proteins CDC20, P55 and fizzy respectively").
The fact that said protein is described as a "plant protein" does not enable it to be characterized either (for example, a human protein of identical sequence to the protein with the SEQ ID No:2 does

VIII. Certain observations on the international application

not appear to be novel over the protein contained in the invention simply because it is of human origin). The combination of the three features ("plant protein", "with WD40 repeat motifs" and "FZR sub-family") does not enable the subject matter of **Claim 1** to be defined clearly, which consequently does not satisfy the criteria of clarity of PCT Article 6. That article, in combination with PCT Rule 6.3(b), specifies that an independent claim must contain all the technical features necessary for the definition of the invention. In this case, the claimed protein must be defined in terms of specific technical features (and not relative to other features), for example its sequence.

2. Furthermore, the heading of **Claim 1** encompasses a whole series of proteins which are similar in some way to the other members of the FZR family without any functional limitation, which may well give rise, in the regional phase of the proceedings, to objections regarding the support thereof by the description (PCT Article 6), the sufficient disclosure of the invention and inventiveness (PCT Articles 5 and 33(3)), and/or lack of unity (PCT Article 13).
The same comment applies to the subject matter of **Claim 11**.

3. It is apparent from the description that the fact that the protein of the invention is that with the sequence SEQ ID No:2 or a similar protein is an essential feature necessary for the definition of the invention. The simple fact of specifying that in

VIII. Certain observations on the international application

the use according to **Claim 11** the protein forms part of the FZR sub-family does not appear to be sufficient: not only does none of the proposed examples describe the use of a gene of the FZR family other than that of the SEQ ID No:1 (lack of support by the description, PCT Article 6), but also, given the well-known differences between plant and animal systems, doubts may be expressed as to whether it is useful to introduce a drosophila gene, for example, in a plant, and as regards the result of such a transformation for the differentiation and proliferation of cells of said transformed plant (PCT Article 5).

Since **independent Claim 11** does not contain this feature, it does not satisfy the requirement of PCT Article 6, in combination with PCT Rule 6.3(b), which specify that an independent claim must contain all the essential technical features necessary for the definition of the invention.

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Translation

PATENT COOPERATION TREATY

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference DB/579	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/FR99/01327	International filing date (*day/month/year*) 04 June 1999 (04.06.99)	Priority date (*day/month/year*) 09 June 1998 (09.06.98)
International Patent Classification (IPC) or national classification and IPC G01J 5/04		
Applicant MOULINEX S.A.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of _____ sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
30 December 1999 (30.12.99)	28 July 2000 (28.07.2000)
Name and mailing address of the IPEA/EP Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/FR99/01327

I. Basis of the report

1. This report has been drawn on the basis of (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

☐ the international application as originally filed.

☒ the description, pages 1-6, as originally filed,
pages _____, filed with the demand,
pages _____, filed with the letter of _____,
pages _____, filed with the letter of _____.

☒ the claims, Nos. 1-10, as originally filed,
Nos. _____, as amended under Article 19,
Nos. _____, filed with the demand,
Nos. _____, filed with the letter of _____,
Nos. _____, filed with the letter of _____.

☒ the drawings, sheets/fig 1/5-5/5, as originally filed,
sheets/fig _____, filed with the demand,
sheets/fig _____, filed with the letter of _____,
sheets/fig _____, filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

☐ the description, pages _____
☐ the claims, Nos. _____
☐ the drawings, sheets/fig _____

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-10	**YES**
	Claims		**NO**
Inventive step (IS)	Claims		**YES**
	Claims	1-10	**NO**
Industrial applicability (IA)	Claims	1-10	**YES**
	Claims		**NO**

2. Citations and explanations

1. Reference is made to the following documents:

D1: WO-A-95/35643 (MOULINEX SA; ARROUBI MUSTAPHA (FR); LEFORGAIS MICHEL BERNARD MAXIM) 28 December 1995 (1995-12-28);
D2: GB-A-2 314 166 (LG ELECTRONICS INC) 17 December 1997 (1997-12-17);
D3: US-A-5 512 748 (introduced by the examiner and attached hereto).

2. The subject matter of Claim 1 does not involve an inventive step (PCT Article 33(3)).

The description states (**see page 1, lines 14 to 24**) that a temperature sensor, comprising the structural features cited in Claim 1 (see description, lines 14 to 24), is already known from the prior art.

Furthermore, efforts to produce more compact systems are well known in the general field of microelectronics. A well-known possibility in that regard is the increased integration of the various components of a system on a single support.

Better integration will be obtained, in particular by incorporating the electronic processing means of a measurement system comprising a sensor, into a support on which said sensor is already located. Document D3 for example discloses integration of this type (see extract and Fig.4, (32) and (62)).

The combination of a sensor already known such as that defined in Claim 1 (lines 4 to 15) with the fact that electronic processing means are incorporated into the semi-conductor material wafer on which a sensitive element (said sensor) is found will easily be anticipated by a person skilled in the art faced with the search for a more compact system and does not therefore involve an inventive step.

3. The following comments relate to the lack of inventive step in Claims 2 to 10.

3.1 D2 also discloses the additional feature defined in Claim 2 (see extract and Fig.4, where the stages (101) and (102) serve to amplify respectively the first and second signals emitted by the sensor and where the circuit (104) creates a signal representing the temperature of a target from the first and second amplified signals).

3.2 Claims 3 to 7 define only features well known in general terms relating to electronic processing systems (amplification stage (Claim 3), adjustable gain (Claim 4), comparator (Claim 5), analog-digital converter (Claim 6), electronic control switch (Claim 7)), which do not produce any unexpected effects.

3.3 Claims 8 to 10 relate only to the use of an infrared temperature detector, the production of which does not involve an inventive step according to paragraphs 2, 3.1 and 3.2, in a household electrical appliance and, in more precise terms, an oven or deep fat fryer (which are well-known household electrical appliances).

These applications are well known (see in particular D1). Consequently, they do not involve an inventive step either.

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

The set of claims does not satisfy the requirements of PCT Rule 5.1(a)(ii) as regards prior art citation (the references to one or more documents, i.e. D1, D2 or D3 for example, must be present).